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Corrosion

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ALSO: Record and Report: A Timely Account of Commerical Developments

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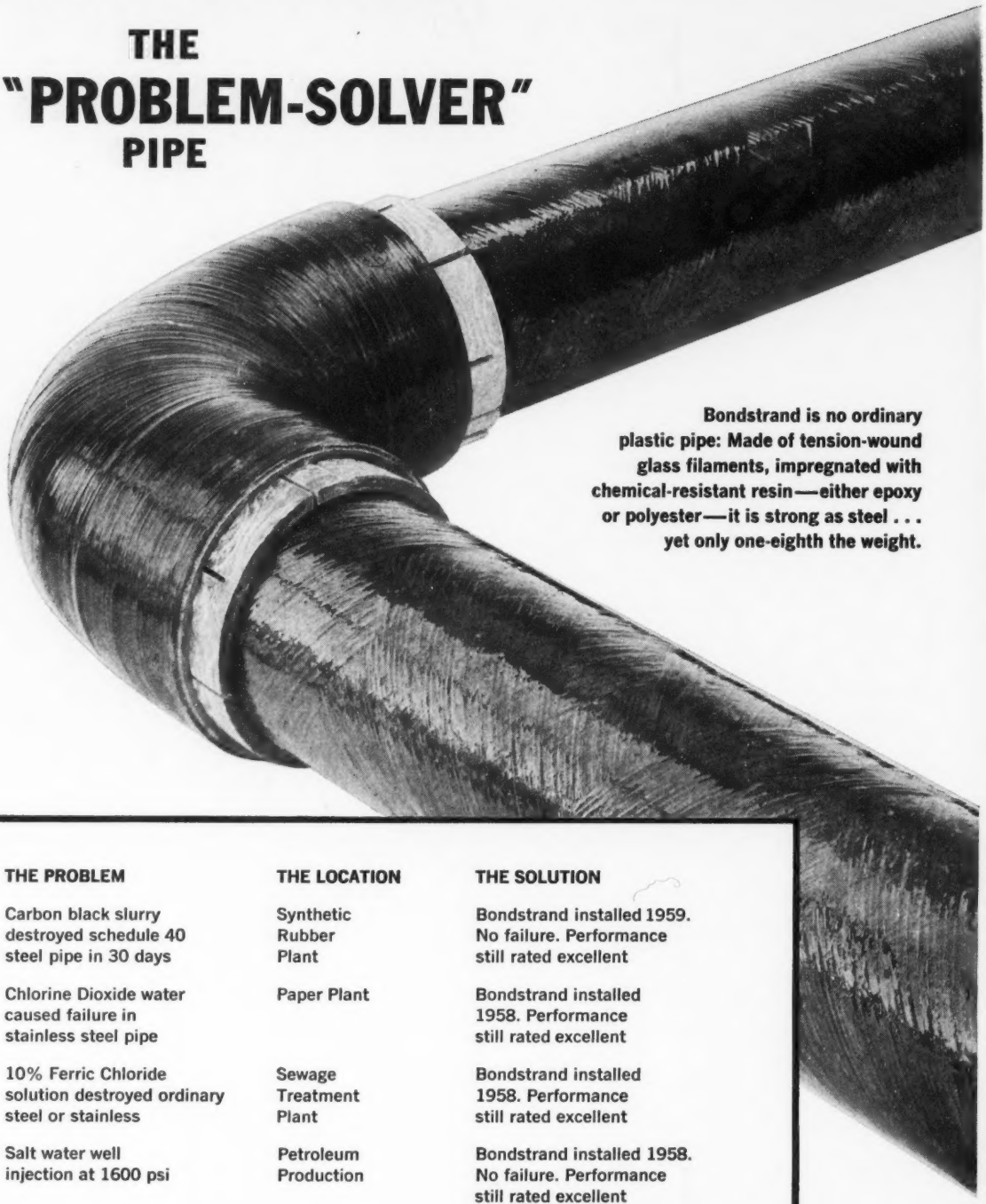

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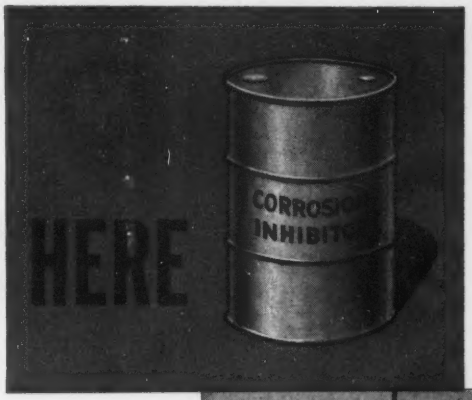

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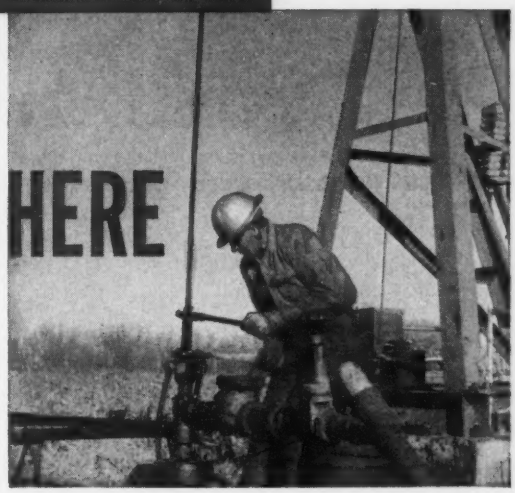

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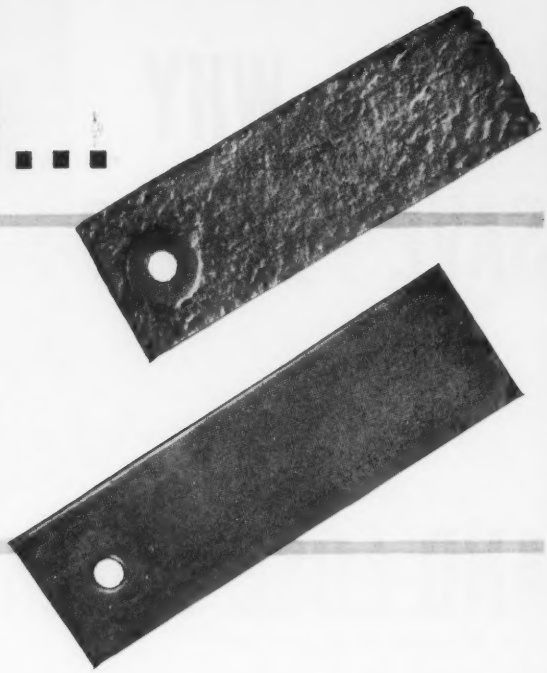

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This Month in Corrosion Control...

A-C CORROSION . . . is there such a thing? This controversial question is covered in this month's editorial on Page 7, considered as to certain data in the literature in a reprinted article beginning on Page 34, and discussed pro and con under the "Letter's to the Editor" heading beginning on Page 60. This is not by any means the whole story on a-c corrosion and there is every reason to hope that useful data will be derived from investigations in the future.

MIXED ACIDS AND ALKALIS in varying proportions and at temperatures to 120 F pose a formidable corrosion control problem. How one chlor-alkali plant solved the problem of disposing of its wastes is described beginning on Page 9.

DESIGNERS AND CORROSION ENGINEERS should get together when a chemical processing plant is being planned so that full weight can be given to corrosion control factors. A method is proposed whereby this can be done through the use of corrosion data sheets covering various classes of equipment, such as heat transfer units, pumps. Turn to Page 14.

CHEMICAL PLANT corrosion control procedures can be made simpler, surer and produce greater savings using a system suggested in an article beginning on Page 19. A peripherally punched control card is shown on which essential information about each piece of equipment can be posted to eliminate guessing and long searches for correct specifications. Extensive tabulated data are given on stress corrosion cracking of commonly used metals.

EXPLOSIONS CAUSED by corrosion damage are reviewed from the viewpoint of the insurance company in an article on Page 22. Basic insurance coverage on boilers is described and case histories are given of three major explosions attributed to corrosion damage. On Page 30 a report on an explosion in a phosphoric acid tank is given.

COOLING TOWERS in a nitrogen plant were treated with a combination of sodium dichromate, phosphate and chlorophenates to reduce excessive corrosion rates. Turn to Page 24.

CHLORIDES CONCENTRATED in some zones of a large nitric acid concentrator from waste products in a uranium refinery caused heavy corrosion damage. Ozone generated by electrical discharge and electrolytic cells are used to convert chlorides into chlorine. Extensive data on numerous corrosion resistant metals in this environment are given beginning on Page 26.

ALUMINUM can be used for ammonium nitrate storage, provided certain precautions are observed. Turn to Page 28.

EPOXY ENCAPSULATED electric motor stators and field windings are protected from corrosives in the environment. An illustrated feature on this development is on Page 37.

CANS CONTAINING FOOD stored in some moist environments soon corrode to cause unsightly discoloration of labels. While contents are not affected, housewives will refuse to buy containers whose labels are discolored in the belief the contents have been stored too long and are either not of best quality or dangerous. Soluble oil containing an inhibitor sprayed on tin plated cans' exteriors improves their resistance to this damage. Turn to Page 75.

HYDROGEN ABSORPTION by zirconium alloys corroding in high temperature water and steam can be reduced by additions of iron, chromium or antimony. These substances may act as depolarizers in preventing hydrogen from penetrating the oxide layer. See Page 81.

PLATINUM-LEAD bielectrodes for cathodic protection are considered in a series of experiments involving the reactions of platinum and lead in chloride solutions. See Page 90.

ALUMINUM ALLOYS' behavior underground is reviewed in both test and experience data. Extensive tabulated data are in the article beginning on Page 97.

CHLORIDE CORROSION and fouling in a catalytic reformer naphtha pretreater initiated studies to determine the effect of pH and composition in the presence or absence of an air atmosphere. High temperature tests were conducted in a nitrogen atmosphere. See Page 105.

HYDROGEN, that culprit common to many corrosive situations, is considered as to mechanism and kinetics in an article beginning on Page 109. The data relate to steel.

WROUGHT ALUMINUM BRONZE was selectively attacked along the weld line and along the fins of a drying drum. Many of the fins broke off after a year's service. Laboratory tests reported in an article on Page 116 established that dealuminization occurred only when chlorides were present in the crevices.

GROUNDING PRACTICES at a large manufacturing plant are described in detail in an article beginning on Page 121 which also considers cathodic protection installations at the plant.

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Corrosion

Published monthly as its official journal, by the National Association of Corrosion Engineers, Inc., at Houston, Texas, U.S.A., as a permanent record of progress in corrosion control.

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AN EDITORIAL

Is There Such a Thing as A-C Corrosion?

PROMPT AND NUMEROUS criticisms followed publication in August, 1960, CORROSION of an editorial titled "Beware of Ground Return Circuits in Electrification." These came from engineers with long experience in corrosion control on power systems. Their arguments were supported by voluminous data of unimpeachable integrity. The criticism which was made with greatest emphasis was that drawing a parallel between the results of direct current and alternating current grounding was not proper and was not justified by the facts. There was general agreement among critics on the following points:

1. The editorial was in error in intimating that corrosion damage like that experienced from direct stray currents was possible from alternating stray currents.

2. Alternating current does not and never has caused corrosion of grounded equipment.

3. A general confession of error on these points should be made.

There is little doubt that the editorial erred in not clearly distinguishing between the known effects of direct stray currents and the probable (and to a considerable degree unproved) effects of alternating stray currents. For this failure, forgiveness is asked.

Not discounting the merits of the arguments against the proposition at all, there is, however, considerable evidence that:

1. Corrosion damage does result from a-c grounding under some conditions.

2. Alternating current does and will cause corrosion under some conditions.

These contentions are supported in part by material included in this issue under the "Letters to the Editor" heading. These data, while certainly not conclusive, show that NACE is not alone, nor the first to be concerned about the possibility of corrosion by alternating currents. Data also show that in certain engineering fields there is a lively interest in the possibility of a-c corrosion and some indication that investigation is needed to ascertain the facts.

If the basic problem can be stated simply, it is this: "Is the effect of alternating polarities on grounded metallic plant completely reversible?" Some data show effects are not wholly reversible.

It is apparently true, for example, also that ferric oxide will rectify alternating currents although at very low efficiency. This must reiterate a basic premise of those contending against the probability of a-c corrosion that this proves that alternating current does not cause corrosion.

Is it not a fact, however, that the alternating currents had to be there before they could be rectified and that they were the primary cause of any corrosion resulting from this rectification?

Arguments are advanced by critics to show that currents induced in a conductor parallel to a power transmission line can be easily and simply drained by proper grounding, provided, of course that the conductor is in contact with the environment. Pipeline engineers point out, however, that in an increasing number of cases, underground conductors are more or less insulated from their environment and that grounding of the induced currents is neither simple nor inexpensive. There probably are numerous other cases where the circumstances are roughly similar.

Power engineers cite the hundreds of thousands of miles of single phase circuits in this and other countries. They correctly point out that they have produced no discernible damage to adjacent underground plant, at least as far as published data and experience go. There is no basis for contending this is not so or will not continue to be so in most cases. The same facts were true when street car systems were first installed.

On the other hand, there is ample justification for an admonition against indiscriminate grounding of alternating current on the basis that it cannot and never will cause corrosion. Conceding that economics will dictate a solution in every case (and this is not peculiar to the electrical current grounding problem), it nevertheless is true that the desirability of providing metal return conductor should not arbitrarily be dismissed without consideration, nor should it be assumed that the conditions which dictate ground return now in a specific case, always will remain the same, unchanged forever.

It is a fact that the people of the world are becoming increasingly urban, and it is a fact that this urbanization already has progressed to a remarkable degree in the United States and that all forecasts point to a continuation. This concentration of populations in urban centers inevitably leads to interference problems with all kinds of electrical emanations. Anything that can be done now to prevent an accumulation of stray currents underground will be to the benefit of all in the future. We think some thought needs to be given to the possible damaging results of draining alternating current to ground. Some reasons for this opinion are given in this issue. We believe also that further investigation will show our concern to be well founded.

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Handling Mixed Corrosives with Glass Reinforced Epoxy Well Tubing and Line Pipe*

David D. Kays
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Wichita, Kansas

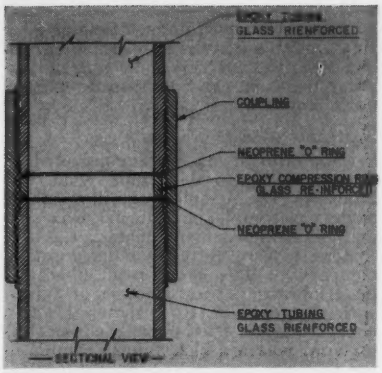

Figure 1—Sectional view of redesigned coupling to eliminate exposed threads. Compression ring in center was used to prevent formation of pockets for concentration of waste.

Abstract

Use of glass reinforced epoxy disposal well tubing and line pipe in a chlor-alkali plant is described. Tubing was used in a well disposing of an average 275 gpm of corrosive wastes at about 120 F maximum including varying concentrations and proportions of hydrochloric, acetic, sulfuric and other acids, sodium hydroxide, sodium chloride, sodium hypochlorite, benzene, chloroform, carbon tetrachloride and other corrosives.

Line pipe was used to handle various concentrations of acids and fume scrubbing liquids at temperatures from 60 to 200 F.

Some difficulties with tubing were reported, attributed to improper joint design, variations in curing and variations in epoxy formulation. Line pipe failures were found to result from inadequate mechanical support and defective jointing, among other probable causes.

Author concludes the glass reinforced epoxy materials are satisfactory under conditions prevailing in his plant where other materials have failed. Some precautions concerning selection are given.

6.6.8, 4.3.2, 4.3.3, 4.4.5

Introduction

PLANTS PRODUCING large volumes of corrosive effluent are faced with significant problems in their disposal. Increasing populations and the growing use of surface water prevent effluent discharge in many cases into flowing streams even when extensively diluted. The problem of disposing of these effluents is handled in many ways including concentration, transportation to remote places for disposal in evaporative ponds and, to a growing extent, by pumping them into geological formations where their presence is not objectionable.

This article relates some experience of the author's company in finding a plastic material suited for such a disposal well and other tests with material of similar composition for line pipe handling various corrosive streams.

In 1957, when plant chemical waste streams reached a volume and composition that made it imperative to dispose of them in a relatively deep geologic formation, an acid resistant tubing in a steel-cased well was selected for an initial test. The steel casing was to be protected by filling the annular space between tubing and casing with oil to prevent corrosive fluids from entering this space at the bottom of the casing.

The search for a tubing with adequate tensile and compressive strength for the service led to glass reinforced, thermosetting epoxy plastic tubing (designated as GRP tubing or pipe in this article). Lack of experience with the widely varying conditions to which the tubing would be subjected dictated the use of 3½-inch OD Grade A performance of this tubing and 4½-inch A and B.

Successful performance of this tubing prompted the use of glass reinforced epoxy line pipe for corrosive fluids in production units. Details of successful and unsuccessful applications are described. Comparisons of the degree of success and length of service life are made between glass reinforced epoxy and other materials such as rigid, nonplasticized polyvinyl chloride (PVC) pipe and asbestos filled phenolic pipe.

In general, the range of application of glass reinforced epoxy to the pipe corrosion problems in a chlor-alkali plant is wide. Limitations described here are field determined and only partially substantiated by laboratory tests.

Glass reinforced epoxy plastic pipe is built up as a centrifugal casting of thermosetting epoxy resin reinforced with glass fabric braid in plies. Both pipe and tubing are furnished in random lengths from 15 to 21 feet. Connecting systems are AST threaded and coupled, flanged 150 psi and 600 psi or 600 psi cemented slip joints with plan end pipe. Threads, where furnished, are molded on finished pipe. Molded fittings are available in either threaded or slip joint style.

Grades are determined by the ability to withstand stresses under specified temperature conditions. For the pipe with which the author is most familiar this variation in grade is a variation in the number of glass fabric plies as well as the wall thickness. There are three grades of pipe and two of tubing. See Table 1 for descriptions and designations used herein.

Chemical Wastes

Beginning in December, 1957, a combined stream of chemical waste amounting to an average of 275 gpm was disposed of in a disposal well tubed with Grade A 3½ inch OD well tubing. These wastes are collected in vitrified clay tile sewers. Flow proceeds through a settling basin with skimming weirs for solids removal. While variations in pH from 1 to 9 in an eight hour period have been recorded they usually are on the acid

(Continued on Page 10)

TABLE 1—Description of Grades of Pipe and Tubing

Designation	Description
PIPING	
A	Premium grade
B	First grade
C	Second grade
TUBING	
A	Heavy service grade
B	Standard grade

★ A paper presented under the title "Glass Reinforced Plastic Pipe and Tubing in Chemical Service" at a meeting of South Central Region, National Association of Corrosion Engineers, Tulsa, Okla., October 25-27, 1960.

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side. Aqueous solutions or suspensions of the chemicals listed in Table 2 are known to be present.

Installation and Operation

The first installation of 4150 feet of 3½ inch OD, Grade A, glass reinforced epoxy well tubing was completed in December, 1957. The annulus charge was diesel fuel with gravity adjusted by the addition of carbon tetrachloride. Before the well was put into operation it was determined that the lower 3000 feet of tubing was separated from the string. This was indicated by the loss of annulus pressure and oil charge. The entire string was pulled and a defective joint removed. The epoxy resin in this one joint of tubing was soft and the glass reinforcing had parted. The tubing had not been subjected to chemical wastes.

After this repair, the well was put in service and operated continuously from December, 1957, to January, 1959. Flow rates varied widely with a maximum of 300 gpm reached occasionally. Annulus pressure varied from 35 to 300 psig. Free chlorine gas was vented from the annulus about 50 percent of the operating time. Tubing internal pressure at the well head varied from 5 to 25 inches of mercury vacuum. Average operating conditions were annulus pressure 35 psig, well head pressure 15 inches, Hg vacuum and flow rate 275 gpm. Fluid temperatures averaged 120 F.

Larger Tubing Substituted

Increasing waste loads made it desirable to install larger tubing in the well. Development of 4½-inch glass reinforced epoxy tubing and the fact that the casing inside diameter would allow its use made it possible to replace the original tubing with the larger size. This was done in February, 1959.

The 3½-inch tubing string was pulled and inspected. Some internal corrosion of the tubing was found later as reported below. Glass fabric was exposed on the bottom joint not protected externally by the annulus oil. A gummy coating deposited on the inside of the tubing varied in thickness from ⅛ inch on the first few joints to a very thin film on the bottom joints. New 4½ inch OD glass reinforced epoxy tubing was assembled with 1400 feet of Grade B on the bottom and 2750 feet of Grade A on top, all supported by a 7-inch wellhead with a special glass reinforced epoxy joint in a carbon steel "doughnut" sealed from the system by neoprene "O" rings.

The well was returned to disposal service in late February, 1959. Flow rates had increased to approximately 400 gpm with acid material still predominating most of the time. Disposal of sulfuric acid on a batch basis was carefully controlled to limit concentration. Other wastes were disposed of without regard to rate or concentration.

Damage Caused by Chlorophenols in Butt Gaps of Couplings

Coupling Failure

No difficulty was experienced until the last week of July (after five months of service) when the tubing string parted at a point in the Grade A portion 1400 feet below the wellhead. Inspection of the string revealed chemical attack and erosion of the exposed interior threads of the coupling between the tubing ends and, to a lesser degree, the exposed ends of the tubing. This lead to a more thorough inspection of the 3½ inch tubing which had been removed earlier and this revealed the same type of attack and erosion, but much less severe than in the 4½ inch tubing. In both strings, attack was not detectable in the tubing itself.

Redesigned couplings were devised to eliminate exposed threads. These were installed and the string was returned to service. Figure 1 illustrates this coupling which incorporates a compression ring to ensure against the formation of pockets for concentration of waste. These couplings have operated continuously for eight months handling the same materials at a rate averaging 400 gpm. Operating pressures and temperatures have not changed appreciably.

Tests and Results

Laboratory tests were conducted in August, 1959, to determine what was attacking the coupling in the tubing string. A sample of material was submerged in the corrosive materials. Three materials were tested for purposes of comparison. The epoxy-resin fiberglass material was a short section of tubing with threads. The PVC material was a short section of PVC pipe. The fiberglass material was a 2-inch square sample of the material used as reinforcing in glass reinforced epoxy tubing and line pipe. Results are listed in Table 3.

These tests indicated that the responsible corrosive agents were chlorophenols from 2, 4-D and pentachlorophenol production. Resistance of the tubing to attack was believed to be the result of the difference between the curing conditions applied to it and that applied to the tubing ends and coupling threads and/or the use of a slightly different resin in the couplings. Concentration of chlorophenols in the gaps left between tubing ends not butted in the coupling was believed to be a principal reason for the damage found.

Line Pipe Applications of Glass Reinforced Epoxy Pipe

Failures of unplasticised polyvinyl chloride pipe (hereinafter designated PVC) and asbestos filled phenolic pipe

TABLE 2—Chemicals Found in Effluent Stream*

Chemical	Concentration Percent
Hydrochloric acid	0—37
Chlorine	Free and dissolved in fluids
Sodium hydroxide	0—50
Monochloroacetic acid	0—5
Sodium chloride	0—25
Sodium hypochlorite	0—10
All chloro-phenols	Trace
Benzene	Trace
Acetic Acid	0—25
Sulfuric Acid	0—5
Methylene chloride	Trace
Chloroform	Trace
Carbon Tetrachloride	Trace
Perchloroethylene	Trace

* Temperatures vary from 60 F to 180 F.

TABLE 3—Laboratory Tests of Three Materials in Corrosive Effluent

Corrosive Liquid	OBSERVATIONS		
	Fiberglass	GRP	PVC
37% HCl with free Cl_2 present	Slight softness, could not pull apart manually	No action on threads could pull strips of fiberglass from outside	No effect.
37% HCl with monochloroacetic acid present	Slight softness, could not pull apart manually	Threads softened slightly. No other action.	Discoloration, no other effect.
37% HCl with free Cl_2 and approximately 0.5% chlorinated phenol from pentachlorophenol primary chlorinator.	Very soft, pulled apart easily, individual fibers weak.	Corrosive action on threads reduced to ½ original height. Softened all epoxy.	Swelling and spongy to touch.
Methylene chloride	No effect.	Threads separating from tube, no other effect.	Swelled and dissolved.
Benzene	No effect.	Threads softened slightly.	Swelled to 3 times original shape.

at about the same time that glass reinforced epoxy pipe became available made it desirable to try it. Application, conditions, approximate footages involved and service life are listed in Table 4. Comments on particular installations follow.

Hydrochloric Acid Production

Glass reinforced epoxy line pipe first installed in this service was C grade 2⅜ inch OD. The installation began at the discharge of the falling film absorber in the producing plant where temperatures are normally controlled to 130 F but occasionally reach 200 F when cooling water to the absorber is limited. The piping system was complete including the run from production to storage, storage to loading facilities and the return of acid to other processes.

Support for the main portion of the lines was on concrete sleepers 10 feet apart. A portion of the line was supported on overhead racks with supports 14 feet apart.

Inspection of leaking pipe after the time indicated in Table 4 revealed a beam type failure for overhead lines with unsupported spans of 14 feet. Failures in the lines supported on sleepers also exhibited this type of failure to some extent but primarily showed internal craze-cracking which indicated that sharp blows or physical crushing may have been sustained. Failure was detected by seepage along pipe sections. No actual attack of the epoxy resin or fiberglass material was detected. The Grade A pipe used to replace the damaged Grade C material has performed satisfactorily although supported on the same structures. The 3½-inch well tubing removed from the disposal well has been put into service successfully as production acid line pipe.

Chlorinator Off-Gas

Grade A 4½-inch OD chemical line pipe was installed as replacement for asbestos filled phenolic pipe to handle off-gas from batch chlorination of acetic acid and phenol. Failure of the asbestos-phenolic pipe resulted in a complete removal of binder and subsequent internal plugging with flaky material. High temperatures were not encountered in this installation because low-temperature condensers precede the piping from chlorinator to fume scrubber.

Service of the glass filled epoxy here was limited, not by failure, but by completion of the production run. Disassembly revealed some softening of the resin after six months' operation.

Fume Scrubbing

Fluid for scrubbing the chlorinator off-gas from batch chlorination of acetic acid and phenol was handled in 3½-inch OD glass reinforced epoxy line pipe. Failure occurred in a relatively short period, the apparent rate being 600 mils penetration per year. The cause of failure was determined by considering the difference between the fluid and the fumes themselves. Sodium hypochlorite,

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TABLE 4—Materials Tested for Line Pipe Service

Material	Service	Corrosive	Operating Pressure	Operating Temperature F	Service Experience
Grade C	HCl production	37% HCl	0—20 psig	60—200	14 months, failed.
PVC	HCl	37% HCl	0—30 psig	60—200	12 months, failed.
Grade A	Acetic-acid and phenol chlorinators	Off-gas	2 in.—20 in. H_2O vacuum	80	6 months, no failure.
Asbestos filled phenolic	Acetic-acid and phenol chlorinators	Off-gas	2 in.—20 in. H_2O vacuum	80	8 months, failed.
Grade A	Chlorinator fume scrubbing	Caustic 0-12% with sodium hypochlorite 0-5%	0—30—psig	120—200	2 weeks, failed.
Impervious Graphite	Chlorinator fume scrubbing	Caustic 0-12% with sodium hypochlorite 0-5%	0—30 psig	120—200	12 months, failed.
Grade A	Liquor decanting from acidification vessel.	30% HCl with traces of chlorophenols and monochloroacetic acid.	0—10 in. Hg. vacuum	140—180	3 months, fittings failed, pipe unaffected
Grade C	HCl transfer	37% HCl	0—30 psig	60—120	14 months, failed.
Grade A					18 months, no failure.
PVC	HCl transfer	37% HCl	0—30 psig	60—120	8 months, failed.

(Continued From Page 11)

high operating temperature and wet free chlorine were blamed. Vinylidene chloride lined steel pipe was used to complete the production run.

Acidification of 2, 4-D Salt

A super natant liquor decanting system for batch acidification of 2, 4-D salt was devised using 3½ inch OD pipe. In this instance, failure was attributed to corrosion and/or erosion of the fittings without severe attack on the pipe, although some softening of the resin was detected. Fittings used in this instance were manufactured from a batch using a slightly different resin than that used in the pipe, according to the manufacturer.

Dip samples were suspended in the acidification vessels for three weeks. No weight loss was detected but the sample of fitting resin became soft while the sample of pipe resin did not. The manufacturer identified them only as the fitting resin and Type A resin which had been used in the pipe. From this test it was deduced that loss of material was the result of erosion after softening.

Field Assembly Methods

Assembly of line piping is more complicated than assembly of well tubing because of the requirements for field cutting, fitting, assembly and supporting of systems. Strict adherence to the manufacturers' recommendations for fitting glass reinforced epoxy pipe and fittings was found to be well worth the effort. Lack of adequate preparation, heating and the use of improper cements invariably resulted in leaking joints. For threaded and coupled pipe and fittings, the use of wrenches designed for glass reinforced epoxy pipe is essential to protect internal surfaces from the craze-cracking resulting from crushing the pipe by applying pressure at two points on opposite sides. A proprietary cement was found to be most satisfactory where another was unsatisfactory, resulting in complete separations before leaks were discovered in several instances. Installations were found to be no more labor consuming than that for PVC and less than for asbestos filled phenolic, using split flange connections. Labor cost compared favorably with that for steel and corrosion resistant alloy piping.

Conclusions

1. The use of glass reinforced epoxy disposal well tubing in a chlor-alkali plant is satisfactory from the corrosion standpoint provided that:
   a. Temperatures are controlled to a maximum of 200 F.
   b. Epoxy resins used to manufacture both tubing and coupling are tested and found to be satisfactory in all fluids to be handled.
   c. Conditions are controlled to give uniform cure for pipe and threaded ends.
   d. Provision is made for periodic inspection at intervals related to experience with materials handled.
2. Glass reinforced epoxy line pipe in satisfactory in the following services:
   a. Hydrochloric acid absorber acid production and all aqueous HCl solutions below 200 F under the conditions existing in the plant experience reported.
   b. Dry organic chlorinator off-gas below 200 F in general and for higher temperatures in selected instances.
   c. Wet chlorine gas below 180 F.
3. Glass reinforced epoxy line pipe is unsatisfactory for handling fluids at temperatures above 160 F which contain sodium hypochlorite.
4. Field installation of glass reinforced epoxy line pipe are no more labor consuming than other plastics and are completely satisfactory if:
   a. Recommended joining methods are followed closely.
   b. Cements capable of withstanding the same corrosives as the pipe are used.
   c. Unsupported lengths are held to the manufacturer's recommendations or less.
   d. Reasonable physical protection from crushing and sharp blows is provided.
5. Service between 200 and 300 F, within the strength limits set by the manufacturer, is satisfactory if the fluid does not soften and erode the epoxy.

In the tests reported here the ability of the manufacturer to control the epoxy material and curing conditions in both pipe and fittings are most important in determining the performance of pipe and tubing.

Acknowledgments

The author is indebted to Frontier Chemical Company for its permission to prepare and present this paper. Assistance of many technical and production people throughout the company was required for its preparation and is hereby acknowledged. Range of application as well as collection of valuable information is due in a large measure to the perseverance of The Fibercast Company and its representatives.

See the April issue for three Technical Topics on highway corrosion problems.

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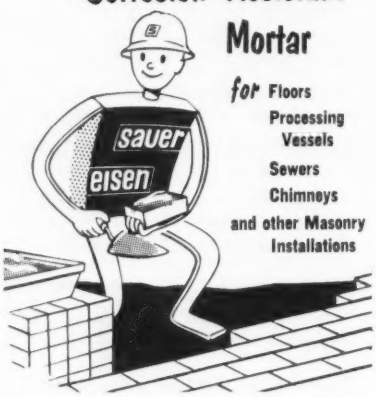

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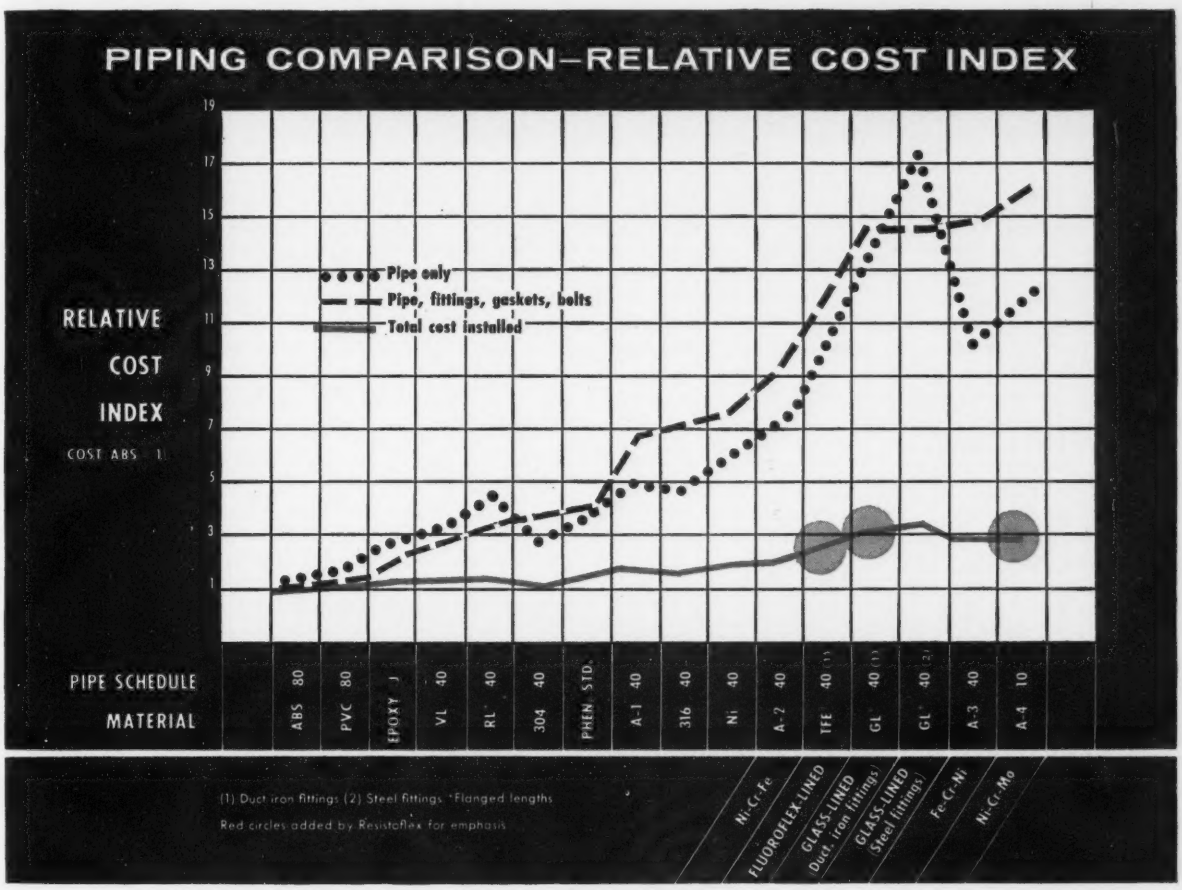

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Corrosion Design Problems in Chemical Process Equipment*

MINIMIZING CORROSION damage in chemical process equipment by correlating corrosion prevention data with chemical engineering design is a practical problem in communications. Frequently the engineering design phase of plant construction is done by engineers who are not experts in the field of corrosion or who have limited knowledge on proper corrosion prevention.

Design engineers hardly can be expected to have knowledge on the hundreds of plastic coatings, paints, metals, alloys plus the vast background of corrosion control practices. Corrosion control has become a complex field requiring specialists.

Because the corrosion specialists cannot always be involved directly in the engineering design of process plants and equipment, some means of communicating their corrosion knowledge and experience to the design engineers is needed.

Corrosion data sheets are suggested and explained in this article as one means of communicating necessary data and information between corrosion personnel and design engineers so that potential corrosion problems can be foreseen during the design phase and thus prevented before the equipment is even built.

This communication problem often becomes an administrative one involving assignment of work to properly qualified personnel who may be in departments completely divorced from the one in which basic engineering is done. In some cases, they may be geographically located at widely separated points. Thus, the communications problem is compounded.

For best results, corrosion preventive design should be started early in the planning of a project. Qualified experts should become familiar with conditions which exist at the beginning. They should have a general knowledge of the process which is selected, raw materials to be handled, nature of the individual streams created in the process, quality of products to be produced, plant site conditions and environmental conditions which might cause corrosion damage.

Communication of all this information to qualified personnel and supervisors must take place in the early stages of engineering design if corrosion control design is to be effective. Long before specifications for equipment are written, data on plant equipment should be carefully studied by corrosion personnel to avoid potential damage and failures.

* Revision of a paper titled "Preventive Corrosion Control in Engineering Design" presented at the Western Region Conference, National Association of Corrosion Engineers, Sept. 29-Oct. 1, 1959, Bakersfield, Cal.

At this point in plant design, however, written information seldom is available to departments or personnel other than those involved directly in the basic design work. To summarize and transmit the required corrosion information, four corrosion data sheets are explained below. The first is one for basic data; the others for heat transfer equipment, pumps and pressure vessels. The sheets on specific equipment are used as examples to show that similar data sheets could be prepared for any equipment.

Basic Corrosion Data Sheet

Obviously, the exact contents of the sheet illustrated by Corrosion Data Sheet 1 can be modified to meet requirements of work being done in particular instances or in specialized engineering projects. However, even the generalized information in the example would provide the basis for a corrosion engineer to decide whether serious corrosion problems could be expected. This basic data sheet would give him indications as to what pieces of equipment to study carefully as the project develops to make certain that problems are foreseen during the design or fabrication steps.

The corrosion engineer should be given the process flowsheet so that he can understand the quantities of materials flowing, their chemical composition, temperatures, pressures and other general information. From this information he can attempt to categorize potential corrosion problems which may eventually be involved in the process.

Heat Transfer Equipment

Because heat transfer equipment frequently is the cause of important corrosion problems, a data sheet is given to illustrate the information necessary on this type equipment (see Corrosion Data Sheet 2).

Because this sheet cannot be completed until the process engineer has written the specifications, a preliminary data sheet—even though incomplete—should be issued so that the corrosion engineer can anticipate corrosion problems that could not be detected previously.

Corrosion Data Sheet 2 could be used for most types of heat transfer equipment excepting fired heaters or furnaces. In these cases, information should be included concerning the fuel to be used and pertinent data on composition and temperature of the stack gases.

From this data sheet, the corrosion engineer can detect conditions which might result in serious corrosion problems related to direct chemical attack, high temperature effects, boiling conditions on surfaces,

Abstract

Explains importance of communications between corrosion engineers and design personnel so that possible corrosion problems can be foreseen and minimized during the design stages of chemical process equipment. Presents four corrosion data sheets as suggested means of obtaining information necessary to the corrosion engineer. Basic data sheet is given plus examples for heat transfer equipment, pumps and pressure vessels. Also explains that data collected for these sheets would not be more than is usually required for design specifications. Emphasizes importance of involving corrosion personnel during the design states of equipment. 5.11

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scale, galvanic problems and high velocity problems. From this information, he can make suggestions to the design engineer so that potential problems can be minimized or eliminated.

The question on existence of mercury in the system (Item 23) may seem irrelevant, but this type situation in process plants frequently is overlooked by design personnel inexperienced in corrosion technology. Cases have been known where aluminum, tin, brasses or other metals capable of being amalgamated by mercury have been used in systems in which mercury was present in such equipment as flow meters. Inadvertent unloading of the mercury into the system during calibration or adjustment of the instrument has caused the mercury to be dispersed throughout the system in fine droplets. Upon contacting metals capable of amalgamation, the mercury has caused punctures with disastrous failure of heat transfer equipment.

This is an example of a corrosion failure which can be prevented through effective use of corrosion data sheets.

Data Sheet on Pumps

Pumps are another type of process equipment in which corrosion damage is common and often has serious consequences. With pumps, the usual corrosion problems associated with construction materials are multiplied by the effects resulting from the pump's mechanical motion and possible reaction with product streams.

Corrosion Data Sheet 3 outlines the information of special importance if corrosion preventive measures are to be taken during plant and equipment design procedures.

Data on Pressure Vessels

Corrosion effects occurring in pressure vessels are some of the most difficult to anticipate because of the nature of the processes involved. But if the corrosion engineer is given the data as shown in Corrosion Data Sheet 4, he can analyze the equipment for potential corrosion difficulties. He will be able to foresee possibilities of direct chemical attack, scaling, concentration cell corrosion due to bubbling and electrolytic effects due to deposits of solids.

The information requested on pressure fluctuations (Item 19 on Sheet 4) may seem unusual but is included because it points to another frequently overlooked source of corrosion difficulties, particularly when coatings and linings are used on the interior

(Continued on Page 16)

Corrosion Data Sheet 1
Basic Information

1. Name of project
2. Owner
3. Geographic location
4. Brief description of process
5. Raw materials
6. Products to be produced (attach specification data if possible)
7. Is this a standard process or is this the first plant of its type?
8. Plant site data: (a) Describe exact location (sea coast, desert, swamp, etc.), (b) Temperatures: maximum summer, minimum winter, (c) Annual rainfall, (d) Maximum wet bulb temperature, (e) Type of soil—dry, sandy, boggy, highly acid, etc. (f) Source of process water, (g) Source of cooling water, (h) Treatment of process water, (i) Treatment of cooling water.
9. Describe degree to which plant will be housed within buildings.
10. Are there any other operations existing or contemplated within the area which will produce vapors, mists, dusts or other effluents which could result in corrosive effects?
11. Comments as to the experience with corrosion already known from existing plants using the same or similar processes.
12. What is length of turnaround period contemplated for this plant?
13. What other scheduled maintenance operations are contemplated?
14. What is payout period used in basic economics for this plant?

Corrosion Data Sheet 2
Heat Transfer Equipment

1. Name of project
2. Owner
3. Geographic location
4. Equipment item number from process flow sheet
5. Type of heat transfer equipment (shell and tube, open coil, etc.)
6. Composition of fluid in tubes
7. Composition of fluid outside tubes
8. Temperature inside tubes: average, maximum and maximum localized skin temperatures
9. Temperatures outside tubes: average, maximum and maximum localized skin temperatures
10. Tube material
11. Shell material
12. Baffle material
13. Tube sheet material
14. Maximum velocities: inside tubes, outside tubes, through baffle holes, at inlet nozzle and at outlet nozzle.
15. Is shell stress relieved?
16. Material of gaskets
17. If pressure relief valves or discs are provided, state materials of construction.
18. Are there any materials of different composition than those already listed that are involved in the structure?
19. Will unit be insulated? If so, give composition of insulation.
20. Will unit be painted or coated? Give composition.
21. Will connecting lines or fittings be of any composition different from that of the heat transfer unit?
22. Nature of solids which may be suspended in the fluids.
23. Is mercury used anywhere in the process, such as in flowmeters or other instruments?
24. What is length of turnaround period contemplated for this equipment?
25. What other scheduled maintenance operations are contemplated?
26. What is payout period used in basic economics for this piece of equipment?

Corrosion Data Sheet 3
Pumps

1. Name of project
2. Owner
3. Geographic location
4. Equipment item number from process flow sheet
5. Type of pump
6. Composition of fluid being pumped
7. Flowing temperature of fluid at inlet
8. Pressures at inlet and outlet
9. Material of case
10. Material of impeller or piston
11. Material of liners, if any
12. Material of shaft
13. Type of seals and material
14. Nature of suspended solids in fluid being pumped
15. Does the fluid consist of more than one phase?
16. Can any gases be disengaged as a separate phase within the pump?
17. Is there any possibility of cavitation on the suction side?
18. Will the unit be insulated? Give composition of insulation and cement to be used.
19. Will unit be painted or coated? Give coating composition.
20. Will connecting lines or fittings be of any composition different from that of the pump?
21. Is mercury used anywhere in the process, such as in flow meters or other instruments?
22. What is length of turnaround period contemplated for this piece of equipment?
23. What other scheduled maintenance operations are contemplated?
24. What is payout period used in basic economics for this piece of equipment?

(Continued From Page 15)

of pressure vessels or on internal parts of such equipment. Pressure changes sometimes cause vapors to be "pumped" back and forth through the microscopic pores of even the best coating. Such action eventually results in the ingress of the fluid, be it a liquid or gas, to the boundary between the coating and vessel's surface. Usually the fluid is corrosive to the surface. Thus corrosion begins under the coating, frequently creating an extremely serious condition because of the concentration effects.

Other Data Forms Suggested

Corrosion information forms can be developed for other types of equipment. The forms given here can be improved or modified or specialized uses. The four forms given as examples can be set up as a uniform system of recording and transmitting basic data for study by corrosion engineers during plant design.

After these corrosion studies are completed, conferences between the corrosion and design engineers should be scheduled so that necessary changes in specifications can be made to minimize the possibility of corrosion. Such conferences also can be used to apply the corrosion personnel's knowledge and experience to proper material selection.

Advantages Obtained From Forms

Use of this system of data forms may seem to put an undue burden on the design engineer and to increase the voluminous paper work involved in normal design procedures. However, these forms do not contain much more information than that normally collected to make proper decisions on material selection.

Most important, however, these forms provide a means of communication between the corrosion engineers and other departments involved in plant design and construction. The forms also provide a basis on which supervisory personnel can make assignment of qualified individuals to the work involved.

Another advantage in using these data forms is that corrosion data can be given to vendors and suppliers who might be involved in the corrosion design problems.

Thus, these corrosion data forms would not increase the total work involved but probably would decrease the total time consumed in making final decisions on equipment design and fabrication to minimize the possibilities of corrosion problems after the plant goes on stream.

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Corrosion Data Sheet 4
Pressure Vessels

1. Name of project
2. Owner
3. Geographic location
4. Equipment item number from process flow sheet
5. Unit operation (fractionation, absorption, extraction, etc.)
6. Composition of fluids: liquid, vapor.
7. Pressures: top and bottom.
8. Temperatures: top, bottom. Are there any points of localized temperature higher than at top?
9. Type of trays
10. Material of shell and material of liners, if any.
11. Material of trays
12. Material of bubble caps
13. Material of hold-down bars, bolts, nuts, etc.
14. Nature of solids suspended in liquids
15. Nature of solids suspended in gases
16. Is shell stress relieved?
17. Will unit be insulated? Give composition of insulation and cement to be used.
18. Will unit be painted or coated? Give composition of coating.
19. What is maximum pressure fluctuation which will occur in vessel?
20. Will connecting lines or fittings be of any composition different from that of the shell?
21. Is mercury used anywhere in process, such as in flow meters or other instruments?
22. What is length of turnaround period contemplated for this equipment?
23. What other scheduled maintenance operations are contemplated?
24. What is payout period used in basic economics for this piece of equipment?

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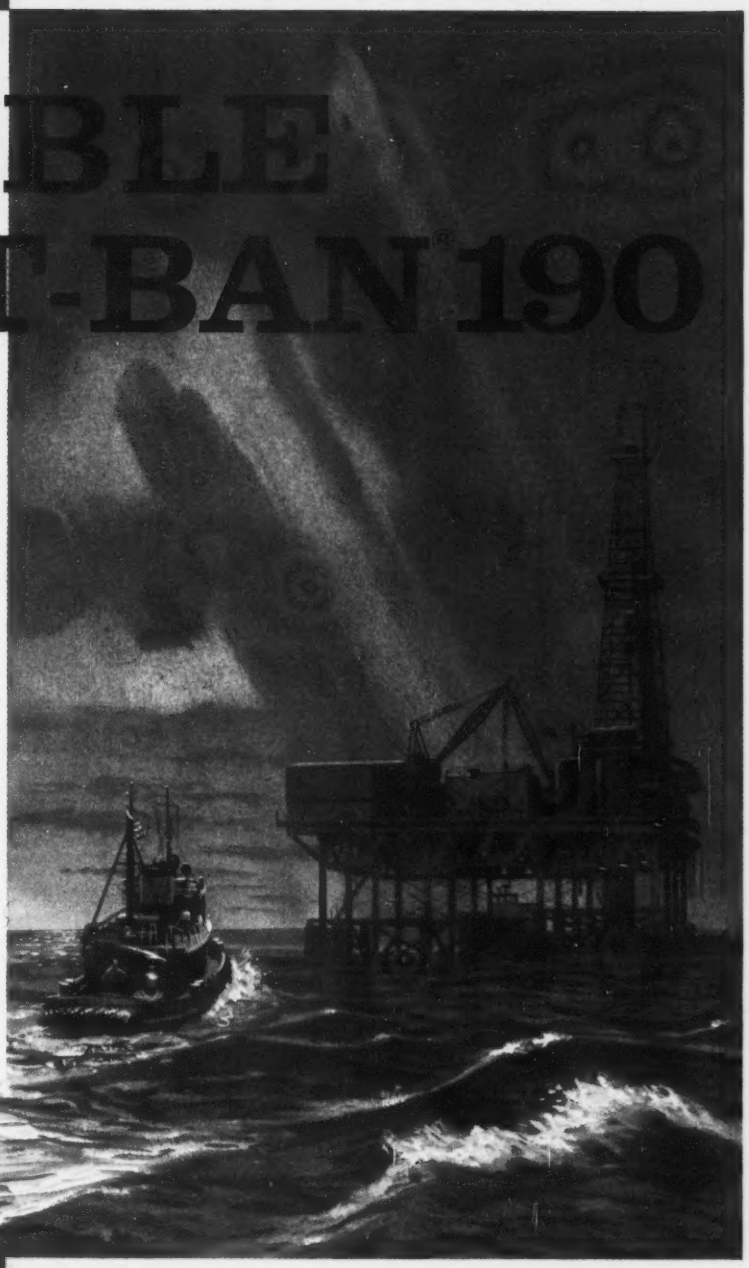

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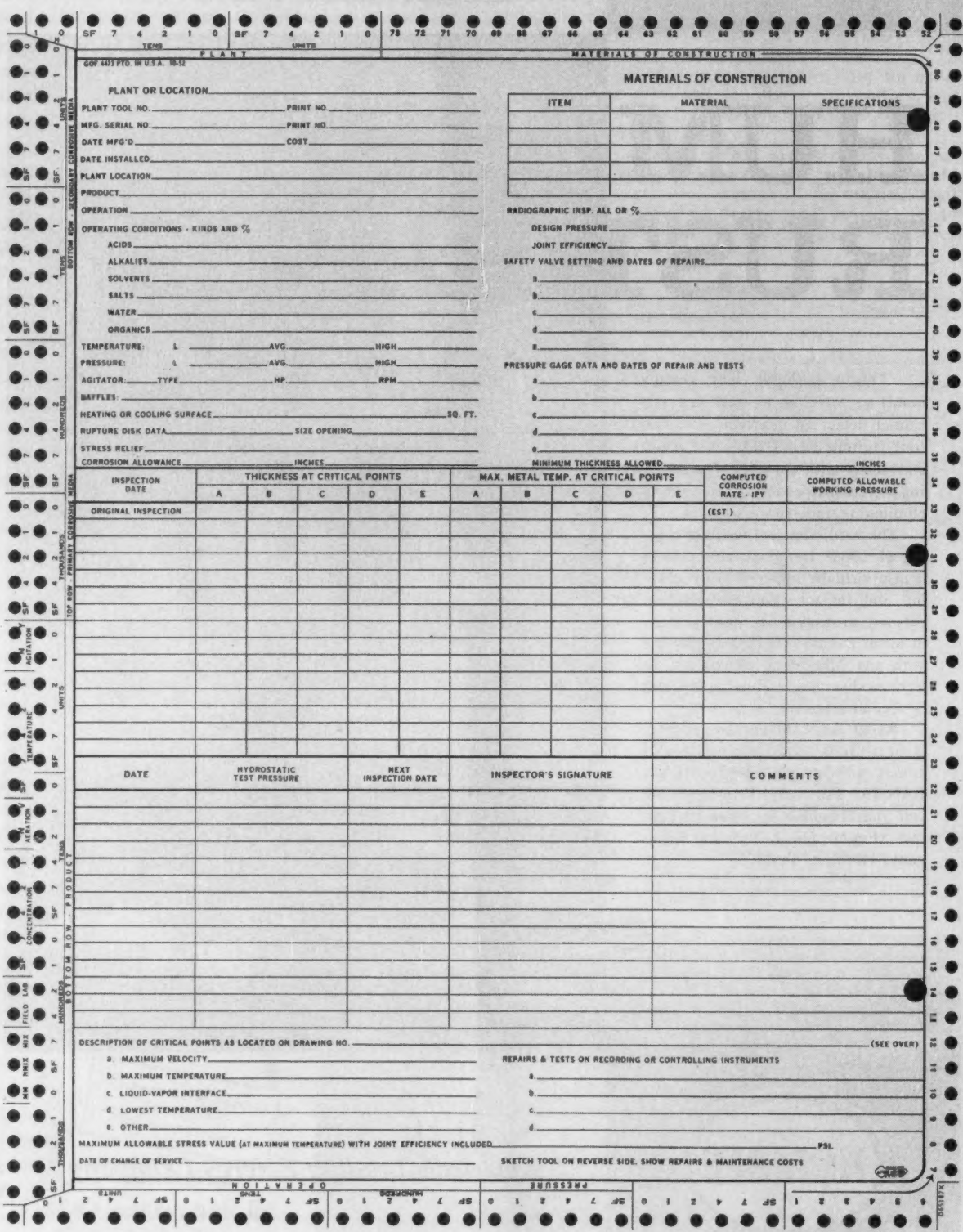

GSF 4075 PTD. IN U.S.A. 10-52

PLANT

MATERIALS OF CONSTRUCTION

PLANT OR LOCATION

PLANT TOOL NO. PRINT NO.

MFG. SERIAL NO. PRINT NO.

DATE MFG'D COST

DATE INSTALLED

PLANT LOCATION

PRODUCT

OPERATION

OPERATING CONDITIONS - KINDS AND %

ACIDS

ALKALIES

SOLVENTS

SALTS

WATER

ORGANICS

TEMPERATURE: L AVG. HIGH

PRESSURE: L AVG. HIGH

AGITATOR: TYPE HP RPM

BAFFLES

HEATING OR COOLING SURFACE SQ. FT.

RUPTURE DISK DATA SIZE OPENING

STRESS RELIEF

CORROSION ALLOWANCE INCHES

MATERIALS OF CONSTRUCTION

ITEM	MATERIAL	SPECIFICATIONS

RADIOGRAPHIC INSP. ALL OR %

DESIGN PRESSURE

JOINT EFFICIENCY

SAFETY VALVE SETTING AND DATES OF REPAIRS

a.

b.

c.

d.

e.

PRESSURE GAGE DATA AND DATES OF REPAIR AND TESTS

a.

b.

c.

d.

e.

MINIMUM THICKNESS ALLOWED INCHES

INSPECTION DATE	THICKNESS AT CRITICAL POINTS					MAX. METAL TEMP. AT CRITICAL POINTS					COMPUTED CORROSION RATE - IPY	COMPUTED ALLOWABLE WORKING PRESSURE
	A	B	C	D	E	A	B	C	D	E		
ORIGINAL INSPECTION											(EST.)	

DATE	HYDROSTATIC TEST PRESSURE	NEXT INSPECTION DATE	INSPECTOR'S SIGNATURE	COMMENTS

Chemical Process Equipment Corrosion*

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Abstract

Reviews general procedures in a chemical plant to recognize and control corrosion. Attention is given to a system which permits keeping data on equipment which may be significant in corrosion studies, including manufacturers' serial numbers, operating conditions, description of materials, schedule of inspection reports, description of critical points and numerous other items all on a peripherally punched card. Specific situations discussed are velocity, liquid-vapor interface, temperatures, test spool data, corrosion by non-uniform attack, stress corrosion cracking and hydrogen embrittlement. 8.8.1

INFORMATION on which the choice of materials of construction in the chemical industry is based comes too often from simulated tests and from the literature. Not nearly enough data come from actual measurement and inspection of equipment in service. Ultrasonic thickness measuring devices[1] make the accumulation of data relatively easy, and the use of the punch card form shown in Figure 1 will make the accumulated data "available" and will pay for itself in lowered inspection costs. When the actual corrosion rates under operating conditions are known, then proper steps for mitigation can be taken readily.

Examination of Figure 1 will show that it covers most of the information required to completely identify the process equipment, operating conditions, corrosive environment in which it operates and the specifications for the materials of construction from which it has been built.

It is convenient to have all this information at hand when equipment is being inspected or evaluated or when replacement is considered. Frequently the actual specifications of the equipment is unknown and assumptions have to be made, including determining minimum thickness for safe operation. Information on joint efficiency is valuable also.

The system is set up so that an inspection is made when the corrosion allowance will be half consumed at the known corrosion rate at the most rapidly corroding areas. When the corrosion rate is unknown, an estimate must be made based on laboratory or pilot plant data or from the literature. In this event, an inspection period based on consumption of one-fourth the corrosion allowance is adopted. After the second inspection has been made, the actual corrosion rate is calculated. The following inspection is scheduled at the end of half the time in which what is left of the corrosion allowance is assumed to last. This procedure is followed until inspections become too frequent to be economical.

When any part of the equipment is corroding at an unexpected rate, the situation is studied for a means to reduce the rate to normal. This may be approached in many ways but Figure 1 is a good guide.

Corrosion Resulting From Uniform Attack

Velocity

If the high rate is found in areas of maximum velocity, perhaps the velocity can be reduced by changing stirrer speeds, increasing pipe sizes or decreasing pump speeds or impeller sizes.

Sometimes impingent plates may be advisable or a wear plate may be installed. If examination indicates cavitation then it may be possible to increase the NPSH (net positive suction head) available for the pump. Lower the temperature or increase the pressure on the system enough to eliminate flashing; or a material more resistant to cavitation may be used as an overlay. If an inhibiting film is being removed, perhaps a better inhibitor, or more of the same inhibitor is in order. Sometimes an inhibitor may be added that will be symbiotic with inhibitors in the stream already and only a very small quantity will substantially reduce attack.

Liquid-Vapor Interface

Another corrosion trouble-spot is the liquid-vapor interface. If this is an area with a high corrosion rate one of the obvious things to do is to eliminate it by having pipe lines run full or in storage tanks vary the level of the liquid-vapor interface as much as possible. By having cylindrical storage tanks and other equipment built so they can be turned readily 180 degrees, life can be almost doubled. Maintenance of a layer of oil or other blanketing material on a liquid surface may eliminate or minimize the interface and vapor phase attack.

The life of sulfuric acid storage tanks can be increased by making the upper half heavier, applying insulation, or putting the tank in a building, so that sun temperature and moisture condensation is reduced. Where the interface fluctuates at nearly the same level most of the time, a belt of more resistant metal or a protective coating may be used. Where the interface attack is increased by water introduced by moist air being drawn into the tank as in sulfuric acid, a submerged breather may be used.

Reducing Temperatures

If the accelerated attack is taking place in areas of maximum temperature or where high temperatures may be suspected, it may be possible to reduce the temperature or to secure more uniform distribution. In one case where an exterior pipe coil was used to heat a tank, the corrosion rate was very rapid at the first coil support nearest the steam inlet. Insulation under this support reduced the "hot spot" and the corrosion rate sharply decreased. Later, installation of an internal heating coil eliminated the problem.

In an installation where high pressure steam was being throttled before being introduced into the jacket of a vacuum dryer, a hot spot developed that was reduced by injecting enough water in the steam to kill the superheat.

The life of a direct fired kettle was considerably increased through the use of a radiant hearth so that hot spots were eliminated.

Because corrosion rates usually are related to metal wall temperature and may be two to four times a base rate after a rise of 50 F, attack may be decreased by lowering the metal wall temperature.

Increasing Temperatures

Sometimes the corrosion rate may be reduced by increasing the temperature. This may eliminate condensates. Or, when they cannot be eliminated, rates found to be very high at 80 C may be much lower at 90 or 95 C because of lowered oxygen solubility.

Low Temperature

An increased corrosion rate because of low temperature usually is a condensate problem. The condensate may be eliminated in some cases by adding insulation or applying heat. A film over the liquid may reduce the vapor pressure. Vapor phase inhibitors or introducing ammonia into the condensate may be used.

Under shut-down conditions if water pH in the system is kept above 9 with NH_3, there will no rusting of steel in the vapor phase or condensate. Steam condensate lines frequently are protected by neutralizing or film-forming amines, and petroleum and petrochemical plants that suffer attack due to water condensates that contain CO_2 and/or H_2S are protected with inhibitors.[2] Tanks or vessels operating below the dew-point should be well painted whether or not insulation is applied.

Test Spools Give Data

If none of these methods reduce the rate of attack to economic levels on common materials of construction, then it is time to consider other materials. One of the best ways to evaluate other materials is to use a corrosion test spool of likely materials.[3] The corrosion rates from this test will be indicative of life that may be expected and the extent to which product contamination may be anticipated.

Corrosion rates so obtained are relative because actual metal wall temperatures may be different and velocity and anodic-cathodic relationships are almost certain to be different. Because corrosion rates may decrease as a function of time it is advisable to use a relatively long test period. It is possible also to evaluate non-metallic materials of construction by much the same method.

(Continued on Page 20)

★ Revision of a paper presented under the title "Corrosion Resistance of Steels: Mitigation of Corrosion in the Chemical Process Industry," at a meeting of Northeast Region, National Association of Corrosion Engineers, Huntington, W. Va., October 11-14, 1960.

Corrosion Resulting From Non-Uniform Attack

(Continued From Page 19)

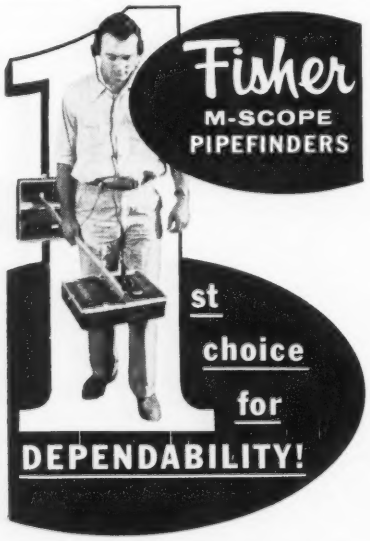
So far considered has been attack of a uniform nature. But because much damage occurs as the result of non-uniform attack, a thorough understanding of factors involved is necessary.

Pitting

Most frequently encountered is pitting and/or crevice corrosion which with cyclic stressing may produce corrosion fatigue. Avoid metals known to pit in certain media, for example, stainless steels in halide solutions. Where it is difficult to avoid them, pitting may be mitigated in stainless steels by a solution heat treatment followed by pickling and passivation. Keep surfaces clean, use reasonably high velocities to avoid deposition of solids. Avoid crevices. Keep chloride solutions away from the shell side of heat exchangers. Increase pH if possible until alkaline. Use molybdenum-containing alloys.

Stress Corrosion Cracking

Table 1 shows a list of metals and alloys and associated environments known to have produced stress corrosion taken from many sources. Avoid these combinations if possible. If they cannot be avoided then equipment should be stress-relieved.



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Under some mild corrosive conditions the hydrogen formed at cathodic areas penetrates the metal lattice as atomic hydrogen instead of forming a polarizing layer. This atomic hydrogen may combine with other atomic hydrogen atoms to form H_2 which develops pressures that may add algebraically with other applied or residual stresses to produce fracture. Hydrogen sulfide and hyrodocyanic acid are among the common supplementary causes of hydrogen embrittlement.

Conclusions

Knowing actual plant corrosion rates make possible the use of inexpensive materials of construction. An organized procedure for mitigating excessive corrosion rates when they are due to controllable factors will keep costs at a minimum. By eliminating all non-uniform attack, maintenance may be kept on a reasonably predictable basis. Organized corrosion testing helps to insure getting the right material in the right place.

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TABLE 1—Some Common Materials and the Environments in Which They Will Be Stress Corrosion Cracked

Alloy	Environment
Aluminum Base	
Al-Zn	Air
Al-Mg	NaCl + H_2O_2 solution, NcCl solution, air
Al-Mg Al-Cu-Mg Al-Mg-Zn	Sea water
Al-Zn-Cu	NaCl, NaCl + H_2O_2 solutions
Al-Zn-Mg-Mn Al-Zn-Mg-Cu-Mn	Sea water
Iron Base	
Mild steel	NaOH solution (15-40%) NaOH + Na_2SiO_3 solutions Nitrate solutions HCN HCN + $SnCl_2$ + $AsCl_2$ + $CHCl_3$ Acrylonitrile + HCN, H_3PO_4, HAc NH_4 Cl solution $CaCl_2$ brine H_2S (prob. wet) NH_4 CNS solution Conc. HNO_3 H_2SO_4—HNO_3 mixture
Fe-Cr-C (400 Series)	Sea water NaCl solution NaCl + H_2O_2 solution NaOH solution NH_3 solution HNO_3 H_2SO_4 H_2SO_4–HNO_3 mixture H_2S (wet)
Fe-Cr-Ni-C (300 Series)	Chloride solutions Sea water Brackish water NaCl + H_2O_2 $EtCl_2$ Wet Magnesia Insulation Crude $NaHCO_3$ + NH_3 + NaCl Na_2CO_3 + 0.1% + NaCl Boiler feed water (concentrated) Crude soda and sulfate pulping liquors Alum solution H_2S Steam (500 °F.) NaOH (15–40%) NaOH solution and sulfur compounds H_2SO_4 + $CuSO_4$ solution H_2SO + Cl^- NH_3 solution Melamine methylation
Fe-Cr-Ni-Mo-C (316–317)	NaOH solution NaOH + sulfur compounds Malamine methylation Chloride solutions H_2SO_4 + $CuSO_4$
Copper Base	
Cu-Al	Steam; NH_3
Cu-Zn Cu-Zn-Sn Cu-Zn-Pb	NH_3 vapors and solutions (CO_2 accelerates)
Cu-Zn	Amines
Cu-Zn-Ni Cu-Sn	NH_3 vapors and solutions (CO_2 accelerates)
Cu-Sn-P Cu-As	Air
Cu-Al	NH_3 vapors and solutions (CO_2 accelerates) (NaCl–Abstracts 1953, Vol. 11, Met. 3)
Cu-Zn-Si	Water Vapor
Cu-Zn-Sn-Mn	Water
Nickel Base	
Monel	Boiling 75% NaOH Organic chlorides (chlorobenzene) Compounds containing Hg Steam over 800 F Hydrofluosilicic acid HF vapors
Nickel	Fused NaOH HCN and impurities Sulfur over 500 F Steam over 800 F HF and hydrofluosilicic acid
Inconel	NaOH solutions at 500-800 F Concentrated Boiler Water 500-800 F Steam and SO_2 HF Concentrated Na_2S
Titanium Base	
Commercial pure	Red fuming HNO_3 (inhibited by 1% NaBr)
Magnesium Base	
Mg-Sn	NaCl + K_2CrO_4 solutions
Mg-Al	Na_2SO_4 or NaCl + K_2CrO_4 solutions
Mg-Al-Zn-Mn	Water
Miscellaneous Metals	
Au-Cu-Ag	$FeCl_2$ solution
Ag-Pt	$FeCl_3$ solution
Pb	Pb $(OOCCH_3)_2$ + HNO_3 solutions Underground Air

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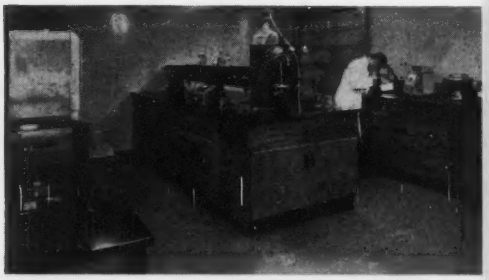

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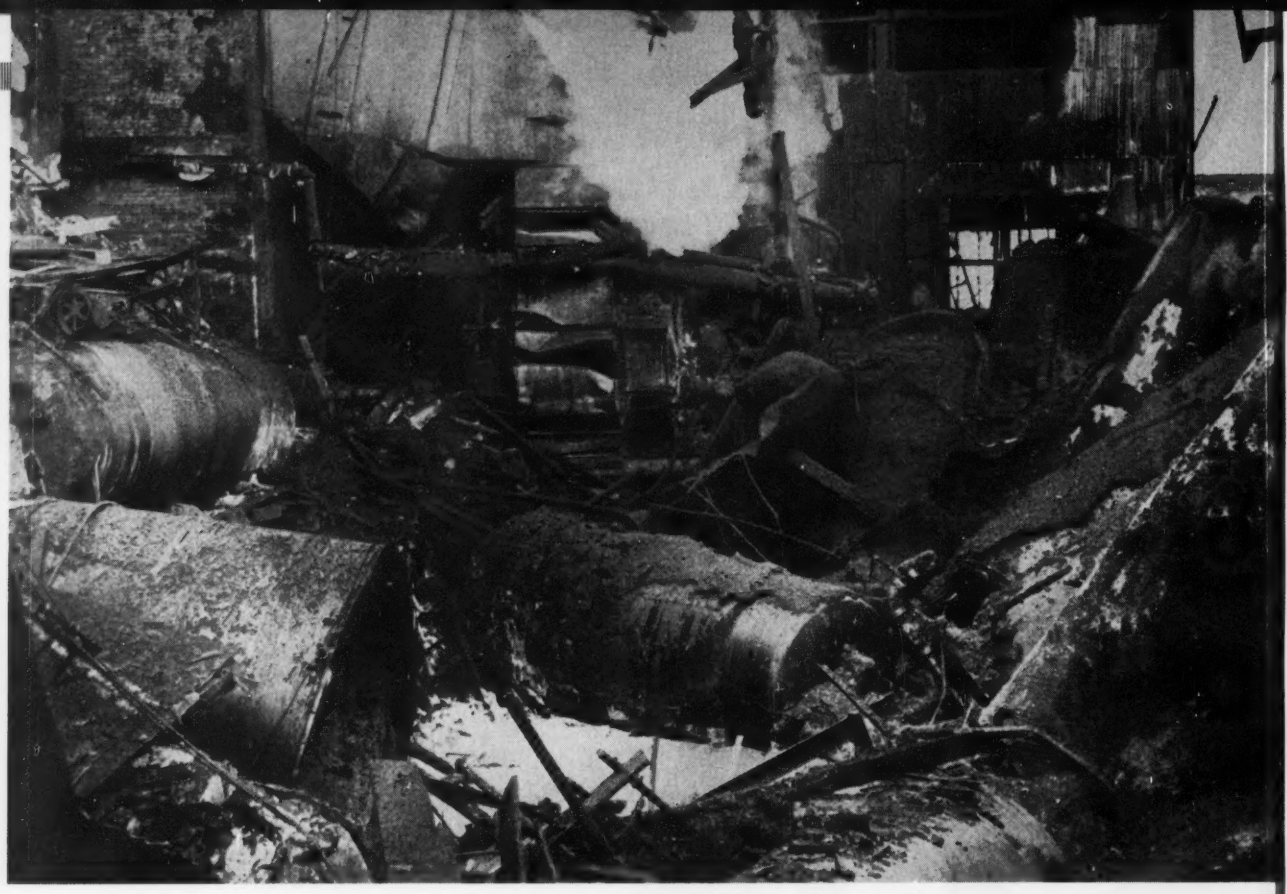

Figure 1—Soda digester that exploded during normal operation completely demolished the digester house, damaged seven other digesters and fatally injured two people. Property damage was over $500,000. Loss was attributed to corrosion failure.

Insurance Company's Viewpoint on

Catastrophic Explosions of Pressure Vessels Caused by Corrosion Damage*

H. M. Canavan

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Waltham, Massachusetts

Abstract

Briefly outlines basic coverage on boilers given by insurance companies. Explains importance of inspection and safety factors. Gives three case histories of major explosions caused by corrosion failure of pressure vessels: soda digester, hot water storage tank and a liquid ammonia and nitrogen storage tank. Emphasizes necessity of knowing rates and patterns of corrosion on equipment to prevent catastrophic failures by proper maintenance, repair or replacement.

1.2.5, 7.6.4, 7.6.6, 7.5.5

Introduction

WHEN INSURANCE is mentioned, most people think of life, fire or automobile insurance. Why is an insurance company interested in corrosion rates of metal? Many insurance companies provide all types of coverage to meet industry's requirements. To give an understanding of why an insurance company providing insurance on boilers, pressure vessels and machinery is interested in corrosion, some of the basic principles of boiler and pressure vessel coverages are outlined below.

Boiler and machinery insurance provides protection against loss caused by defined accidents to a variety of equipment which come under the general categories of boilers, pressure vessels and power equipment. Examples include watertube and firetube boilers, digesters, blow tanks, autoclaves, paper machine dryer rolls, air tanks, etc.

Boiler Insurance Coverage

The basic insuring agreement provides direct damage insurance on boilers and pressure vessels described in a schedule, either specifically or by named group, attached to the policy. Provisions of the basic policy apply to loss resulting from an accident to any insured equipment during the policy period and while equipment is in use (or connected and ready for use) at the location specified.

The basic insuring agreement includes six coverages:

Coverage A—Direct damage on property of insured caused by an accident. "Property of the insured" includes not only the equipment (usually referred to as "object") insured under the policy schedule, but also any other property of the insured. In addition, includes contents of the object to a limit of $1000, which may be increased by an additional premium.

Coverage B—Expediting expenses incurred for temporary repairs to stop leakage from a cracked section of a cast iron boiler or to hasten repairs by paying overtime to repairmen or by requesting shipment by air for rapid delivery of parts. This coverage is subject to a limit of $1000 or an amount equal to

★ Extracted from a paper titled "Corrosion and Its Relationship to Boilers and Pressure Vessels From an Insurance Company's Viewpoint" presented at the North Central Region Conference, National Association of Corrosion Engineers, October 19-20, 1960, Milwaukee, Wis.

the loss under Coverage A, whichever is less.

Coverage C—Damage to property of Others for which the insured is liable, including loss of use of property.

Coverage D—Bodily injuries (optional) for which the insured may be legally liable, excluding liability under any workmen's compensation law. This does not apply to any portion of loss covered by any other insurance. This coverage also pays for emergency medical and surgical relief at the time of the accident, payment being in addition to and not part of the specified limit per accident.

Coverage E—Defense of the insured against all claims and suits including premiums on appeal bonds, expense of suits, interest accruing after judgment, all in addition to the specified limit per accident.

Coverage F—Automatic coverage, subject to written notice within 90 days, on any similar object which is newly installed at any location specified in the policy or which is located on any newly acquired property.

Coverages described have been applicable only to direct damage. Even more serious losses of an indirect nature, such as loss of production and product spoilage also can result from accidents to boilers and machinery. Therefore, coverages for these exposures are available through the following endorsements: use and occupancy insurance, outage insurance, consequential damage insurance, power interruption insurance, excess demand charge coverage and extra expense coverage.

Any loss is subject to conditions of the insuring agreement and definitions of accident. The term "definition of accident" varies with different kinds and types of equipment with each occurrence being sudden and accidental.

This brief outlines does not describe all available coverages, conditions applying to the insuring agreement, declarations or endorsements.

Role of Engineering

Engineering plays a definite and important role in boiler and machinery insurance. Basically, engineering is concerned with conservation of human life and property. Specifically, insurance engineering is concerned with prevention of accidents covered by insurance and which can be reduced or eliminated by application of engineering knowledge and experience.

Insurance engineering requires the services of trained men qualified by education, experience and ability to determine the safety and dependability of structures and operations. Engineering codes have been developed that require pressure vessels to be designed with adequate safety factors. Codes also establish the minimum number of required operating devices and safety valves to protect vessels against overpressure. However, after vessels have been in service and loss of metal occurs from corrosion during normal operation, then a problem of inspection and maintenance at the site is encountered. The inspector's first concern is safety, but his primary objective is to find the corrosion, determine the percentage of metal left in the corroded area and to establish a safe working pressure.

Pressure vessels fail as a result of being weakened by corrosion. Numerous corrosion failure cases involving major explosions have resulted in loss of life and extensive property damage. Failures of this type usually occur at normal operating pressure. Therefore, safety devices are not important in preventing these losses. As a result of these corrosion failures, an insurance company can have direct and indirect damage losses involving thousands of dollars.

Three Case Histories of Corrosion Failures

Three case histories are given to show what catastrophic accidents, property damage and loss of life can result from corrosion failures on boilers and pressure vessels.

In 1951, a soda digester, 84 inches by 22 feet, exploded during normal operation and completely demolished the digester house, damaged seven other digesters and fatally injured two people. (See Figure 1.) The accident occurred at night; many more people would have been injured if the explosion had occurred during the day. Property damage was over half a million dollars. The plant was idle for about a year. Investigation revealed that corrosion had reduced the shell thickness by more than 50 percent, thus causing the failure.

Another case history is a hot water storage tank, 48 inches by 15 feet, which exploded in 1952 while operating under normal conditions. The building was completely demolished. Property damage was about $100,000. (See Figure 2.) Investigation again revealed that internal corrosion had reduced the plate thickness by over 50 percent.

A liquid ammonia and nitrogen storage tank can be cited as another case of sudden and dramatic corrosion failure.

(Continued on Page 24)

Figure 2—Hot water storage tank exploded while operating at normal conditions. Internal corrosion had reduced plate thickness by 50 percent, thus causing the catastrophic failure which resulted in property damage of about $100,000. The building was completely demolished by the explosion.

Figure 3—Property damage of about $50,000 resulted from this liquid ammonia and nitrogen storage tank which exploded on a tank farm. Failure was caused by internal corrosion which had reduced the original shell plate thickness by 50 percent.

Water Treatment Change Reduces Nitrogen Plant Corrosion Rates*

CORROSION TESTS on the hot water return to the cooling tower in a nitrogen plant showed the corrosion rates on mild steel to be 10 to 15 mils per year. For these tests, a piece of jacketed steel pipe was placed in the system so that the test pipe was heated with steam to maintain active heat transfer as the water passed through.

Although the corrosion rates were high and probably would have caused heat exchanger problems a shutdown occurred because of other reasons.

Considerable difficulty was experienced in eliminating algae growth on the top deck of the cooling water during the initial start-up of the plant. This area was under optimum conditions for good algae growth with adequate sunlight and desirable water temperature. Large quantities of chlorine were necessary before adequate algae kill was obtained. Physical removal was accomplished only by brushing the algae growth loose and letting it fall into the cooling tower basin.

Another problem was the special cleaning of the exchangers during the shutdown to remove the scale.

After this shutdown, water treatment was drastically altered to maintain 300 ppm of sodium dichromate and about 10 ppm of phosphate in the cooling water system. Chlorination of the water for algae control was replaced by the use of chlorophenates on an intermittent basis. Regulation of concentration cycles has not been necessary because normal water losses maintain the desired level of total solids.

After this change in the water treatment, corrosion rates dropped below 3 mils per year. Also, inspection of exchangers throughout the plant showed that scale formation had been controlled to such an extent that further cleaning of the exchangers was not required. And there were no evidence of excessive corrosion in any of the exchangers.

Cost of this altered water treatment was in line with the average costs of plants using similar type treatments. Some cost reduction could be made by reducing the treatment level, but the company believes the relatively small amount of money used in excess chemical treatment is good insurance against corrosion and scaling which could result in expensive downtime and income loss.

★ Extracted from a paper titled "Corrosion Considerations in a Fertilizer Nitrogen Chemical Plant" by Robert T. Lukat, Southern Nitrogen Company, Inc., Savannah, Ga., presented at the Southeast Region Conference, National Association of Corrosion Engineers, October 6-8, 1960, Atlanta, Ga.

Explosions—

(Continued From Page 23)

Measuring 108 inches in diameter by 39 feet, this tank exploded in 1953, with a resulting property damage of about $50,000. Fortunately, the tank was located in the open on a tank farm. (See Figure 3.) Here again, internal corrosion had reduced the original shell plate thickness by over 50 percent.

Importance of Corrosion Rates

Areas of equipment in which corrosion is occurring must be located by inspection, and the pattern and rate of corrosion must be determined. Stress cracking, which can progress to the point of failure, can be accelerated by corrosion. Pits caused by corrosion become the foci of stresses which in turn cause cracking.

A valid estimate of the corrosion rate permits repairing or replacing a section of equipment in time to be sure the equipment retains the same maximum allowable working pressure and safety factor. Persons responsible for operation and safety can plan for repairs or total replacement of the unit if the corrosion rate is known.

The inspector from the insurance company is a specialist in safety—not a process expert. He can assist in determining causes of corrosion and can make corrosion control suggestions. If he considers it necessary, he will recommend the specialists in the particular field involved be contacted for advice.

Accident prevention and inspection services provided by boiler and machinery insurance companies are an important factor in keeping manufacturing costs down. Benefits of loss prevention are difficult to evaluate in dollars and cents. Unfortunately, catastrophic failures make the news—not the successes in preventing accidents.

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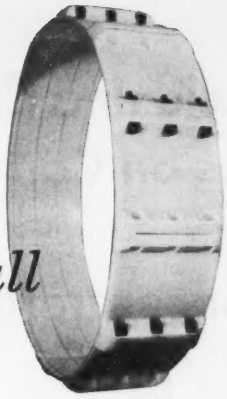

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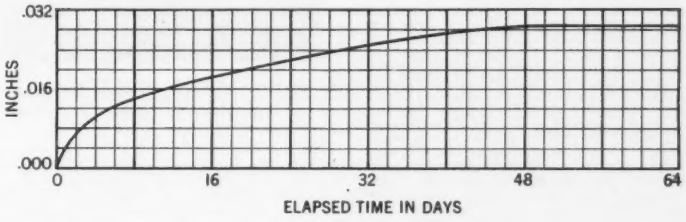

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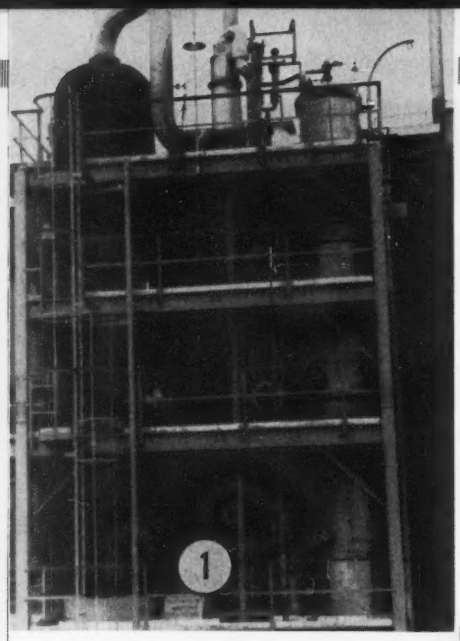
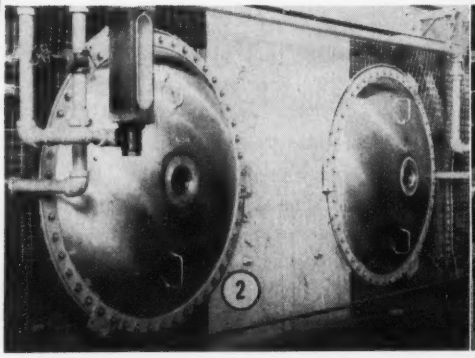


Figure 1—Dark colored vessel at left is nitric acid concentrator.

Influence of Acid and Chloride Concentrations on Corrosion in a Nitric Acid Concentrator*

J. B. Lowe
Eldorado Mining and Refining Ltd.
Port Hope, Ontario, Canada



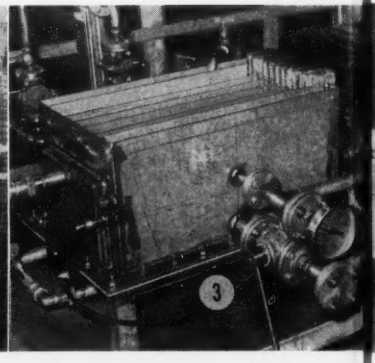


Figure 2—Electrical discharge ozone generators. Figure 3—Electrolytic cells used to convert chlorides into chlorine for exhaust in gaseous effluent. Hood removed, anodes in place.

Abstract

Experience with corrosion in a large concentrator used to recover nitric acid from raffinate waste products in a uranium refining plant is related. Solution of the corrosion problem in the concentrator involved generation of ozone by electrical discharge generators to oxidize chlorides to produce chlorine. An electrolytic cell also has been used to remove chlorides. Chlorides concentrate in that portion of the tower where acid concentration is 20-30 percent, necessitating frequent replacement of bubble caps and other parts. Areas subjected to high velocities had abnormally high corrosion rates. Results of tests on Hastelloy C, Carpenter 20, Ni-O-Nel, Incoloy, Inconel and various stainless steels are tabulated for 25-35 percent acid strength with 550 ppm chlorides; at 30-40 percent acid and 800-900 ppm chlorides. A table gives a corrosion profile of the concentrator from Trays 1 through 12 in both acid and vapor phases. Several conclusions are listed including one that chloride removal by electrolysis is not more efficient or less expensive than by ozonation until concentrations exceed 1000 ppm. 18-8 series stainless suffers negligible corrosion up to 200 ppm chlorides, and tolerable rates when chlorides are below 600 ppm at low flow velocities. At chloride concentrations over 900 ppm corrosion of 18-8 is excessive. 3 tables, 9 figures.

4.3.2, 7.6.5

Introduction

THE MODERN method of refining uranium by solvent extraction is carried out in pulse columns or similar equipment. The waste product from this process, called raffinate, contains numerous metallic nitrates from which nitric acid used for dissolution of the concentrates is recovered. Sulfuric acid "Springing" and evaporation of the waste raffinate, is carried out to release quantities of dilute nitric acid vapors to the recovery system. This process also releases chlorides which form a highly corrosive mixture in the concentrator when mixed with the nitric acid.

Coping with this problem involves 1. Keeping chlorides in the feed material to a minimum. 2. Providing both ozone generators and electrolytic cells in chloride removal. 3. Relying on experience and economics in selecting materials for fabrication of recovery equipment.

★ Revision of a paper titled "Corrosion in a Nitric Acid Recovery System Due to Presence of the Chloride Ion" presented at a meeting of the Canadian Region, Eastern Division, National Association of Corrosion Engineers, January 18-21, 1950, Toronto, Ontario.

Operation and Description of Facilities

1. Recovery Equipment

The nitric acid concentrator shown in Figure 1 made of Type 347 is 32 feet high and has an internal diameter of 5 feet 6 inches. The lower five feet of the tower is used for surge volume and to provide sufficient hydraulic head for operation of a thermosyphon reboiler made of Type 309 CB.

There are 12 bubble cap trays with 63 caps on each at 24-inch spacing in addition to inlet and outlet weirs and a 6-inch downcomer. These are discussed in detail later. Vapor feed to the tower from the raffinate evaporator is introduced between the second and third trays and is contacted by a countercurrent flow of reflux water.

An overhead water condenser and steam ejector provides vacuum (28-inch Hg absolute) for the tower. This lowers the temperature within and thereby reduces the rate of corrosion. Pumps and piping are provided to withdraw high chloride acid from trays 3 to 6 and return it to the column after chloride removal.

Nitric acid of 55-60 percent strength, having been concentrated by fractionation, is withdrawn from the bottom of the tower for reuse in the digestion area.

2. Ozone Generators

Ozone for oxidizing the chlorides is generated in industrial type, electrical discharge generators from clean dry air. See Figure 2. Three units produce approximately 90 lb. of ozone per day. The air stream emerging from the units contains about 1 percent ozone by weight.

This ozone-air mixture at 8 psig then is dispersed by diffuser tubes in the bottom of a Type 304 ozonation tank. As the ozone-air mixture ascends through the chloride-contaminated nitric oxidation of the chloride by ozone occurs. Chlorine formed in this reaction then is carried out in the effluent gas from the ozonation tank and discharged to the atmosphere.

This process, although relatively new, is widely used for such oxidation reactions and requires that the acid be heated to 175 F for most efficient operation. Heat exchangers of Type 316 have been used in this service with piping of either Types 304 or 347.

These facilities permit treatment of 60-180 Imperial gallons per hour of chloride-contaminated acid with an overall removal efficiency in the range of 20-65 percent. As the concentration of chlorides in the feed material increased, existing equipment soon was severely attacked by corrosion. The company's research and development group carried out investigations to improve the facilities and to find other ways to attack the problem. Their work resulted in

higher ozonation efficiencies and development of an electrolytic method of chloride removal.

3. Electrolytic Cells

The electrolytic method employed and the cell design all were developed by Eldorado Mining and Refining Co. So far as the writer knows, his is the only company using this means to remove chloride from nitric acid.

The production unit (Figure 3) employs copper cathodes and platinum anodes. Figure 4 shows the anode and Figure 5 a detail on the platinum unimesh employed. The original copper cathodes, shown in Figure 6, have been modified so that immersed plates can be replaced easily if necessary. Both cathodes and anodes are protected above the liquid level by an encasement of acrylic or polyester resin.

The cell and its cooling tubes are fabricated from Type 304 which so far have shown no appreciable corrosion.

Bubble caps made initially of Type 347 used a threaded connection for positioning above the tray. Nuts and threaded components were preferentially attacked, making them loose and out of position. New designs made it possible to tack-weld the caps directly to trays.

Those portions of the downcomers and caps exposed to the vapors had a much higher rate of corrosion than those immersed in the acid. Areas subject to high velocities suffered abnormally high corrosion rates. This was noted on pump impellers, in transfer pipe lines and in the internals of bubble cap risers. See Figure 9.

Table 1 shows that Type 304 is more resistant to 20-30 percent nitric acid containing 515 ppm chloride than Type 347 is. Table 2 shows results of increasing the chloride content of the acid to 800-900 ppm. At this concentration the corrosion rate of Type 304 increased 147 times over that at the lower figure, making it one of the least resistant alloys. These tables show the highest corrosion rates in the vapor phase, with few exceptions.

Table 3 shows a typical corrosion profile over the column with average chlorides in Tray 3 through 6 at 634 ppm. These determinations apply to the Type 304 alloy with exposures to variable acid strengths, namely, 5-10 percent on Tray No. 12 and 55-60 percent on

(Continued on Page 28)

TABLE 1—Corrosion Rates at 25-35 Percent Nitric Acid With Chloride Average 515 ppm

Acid strength—Variable in range of 25–35 percent.
Period—92 days (December 31, 1957 to April 2, 1958)
Temperature—155–165 F.
Aeration—Nil
Agitation—Slight
Location—Vicinity tray No. 4
Samples—International Nickel Co. of Canada Ltd.

Alloy	Corrosion Rate ipy	
	In Acid	In Vapor
Hast. C	.0241	Corroded away
Carp. 20	.00045	.00068
Ni-O-Nel	.00046	.00096
430	.00051	.00133
321	.00049	.00099
347	.00038	.00072
310	.00018	.00043
316	.00045	.00106
309	.00021	.00045
304	.00026	.00057
Incoloy	.00175	.00263
Inconel	.00825	.0230

TABLE 2—Corrosion Rates at 30-40 Percent Nitric Acid With Chloride Average of 800-900 ppm

Acid strength—Variable 30–40 percent
Period—148 days (August 5 to December 31, 1959)
Temperature—Varied, depending on location in tower
Aeration—Nil
Agitation—Slight
Location—Vicinity Tray No. 3
Samples—International Nickel Co. of Canada Ltd.

Alloy	Corrosion Rate ipy	
	In Acid	In Vapor
Carp. 20	.00040	.00073
Ni-O-Nel	.00041	.00085
430	Corroded away	Corroded away
321	.00103	.00757
347	.02460	Corroded away
310	.00010	.00201
316	.00769	.01420
309	.00037	.00177
304	.03810	.0241
Incoloy	.00135	.00840
Inconel	Corroded away	Corroded away

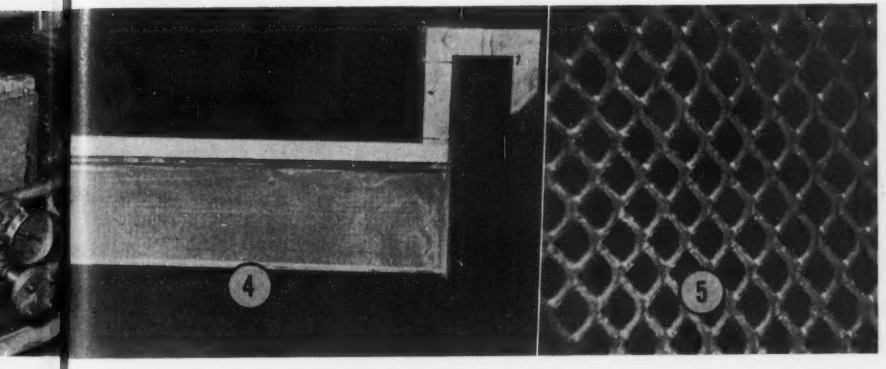


Figure 4—Platinum anodes used in electrolytic cell. Figure 5—Close-up of platinum unimesh used in cell.

The acid is precooled before it enters the cell and its temperature further reduced to 75 F maximum by the internal cooling tubes. Across the bottom is a porous Carborundum plate to the underside of which 7 cfm of air per cell is admitted for agitation and to aid in sweeping the electrodes free of hydrogen and chlorine. Exhaust systems (Figure 7) are used to vent these gases to atmosphere.

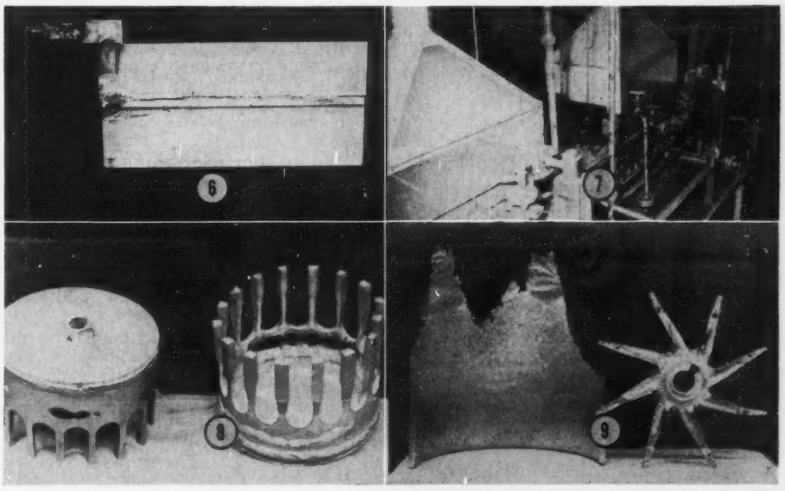
A selenium rectifer supplies 2.8-3.2 volts of direct current to each cell at a current density of 55 amp/ft². Standby power is provided by a battery installation equipped for automatic switching.

The two cells have optimum capacity of 45 Imperial gallons per hour and an overall removal efficiency of 25-60 percent at design flow rates. Nine months of operations show that control of acid strength and temperature is a necessity for long cathode life. Plating of metallic impurities on the cathodes sometimes takes place but these can be removed by a temporary power interruption which allows them to redissolve in the acid.

Nature and Location of Corrosion

Most of the chlorides driven into the recovery system concentrate in that portion of the tower where the acid strength is in the range of 20-30 percent. This area experiences worst corrosion, requiring frequent replacement of bubble caps, downcomers and other components. See Figure 8.

Figure 6—Copper cathodes used in electrolytic cell. Figure 7—Showing exhaust system used over electrolytic cells to vent gases to atmosphere. Figure 8—Corroded caps from regenerator. Figure 9—Section of downcomer tube and pump impeller, showing the effects of velocity on corrosion.



Nitric Acid–

(Continued From Page 27)

Tray No. 1. Trays are numbered beginning at the bottom.

This report is based on five years of plant operation and results reported may not be reproducible by laboratory methods. Not mentioned or accounted for are such variables as (1) trace compurities in the acid (2) upset operating conditions (3) upper and lower limits of chloride content.

Conclusions

1. Past experience indicates that alloy resistance to nitric acid contaminated with chloride is dependent upon (a) temperature (b) chloride content (c) acid strength (d) velocity effects (e) length of exposure.

2. Test coupons indicate that vapor phase corrosion rates are higher than corresponding liquid phase corrosion rates excepting a few alloys.

3. Experience indicates that cast forms of 18-8 stainless steels are much more susceptible to corrosion by nitric acid and nitric acid-containing chlorides than comparable wrought forms.

4. Wherever possible exposed "end grains" should be seal welded to prevent end grain attack.

5. Eldorado's limited experience indicates that chloride removal by electrolysis is not more efficient or less expensive than ozonation methods based on the unit cost to remove a pound of chloride until concentrations exceed 1000 ppm.

6. Generally speaking, a recovery system as described and fabricated of 18-8 steels suffers negligible corrosion up to 200 ppm chloride. When chloride levels are stabilized below 600 ppm corrosion rates of 18-8 steel, when the stream is moving at low velocities, are in the range of .0003 to .0008 ipy.

7. When chloride concentrations approach or exceed 900 to 1000 ppm, the corrosion rates of the 18-8 stainless steels become excessive by Eldorado standards and consideration is given to other alloys.

8. In designing nitric acid recovery equipment for maximum corrosion resistance, consideration should be given to design changes minimizing velocity effects.

TABLE 3—Nitric Acid Corrosion Profile of Type 304 Stainless Steel in Concentrator

Acid Strength—5–10 percent on Trays No. 12 and 55; 60 percent on Tray No. 1. Other trays in proportion.
Period—174 days (April 3 to July 21, 1958)
Temperature—Varied, depending on location (Tray No. 1: 175 F; Tray No. 12: 115 F)
Aeration—Nil
Agitation—Slight
Location—In acid and vapor of all 12 trays.
Samples—International Nickel Co. of Canada Ltd.
Average chloride—Trays No. 3–6 approximately 634 ppm. Proportionately lower on other trays.

Tray No.	Corrosion Rate ipy	
	In Acid	In Vapor
1	.00050	.00067
2	.00045	.00039
3	.....	.00038
4	.00022	.00037
5	.00014	.00023
6	.00058	.00108
7	.00016	.00022
8	.00023	.00014
9	.00024	.00020
10	.00024	.00012
11	.00015	.00030
12	.00024	.....

If Precautions Are Taken

Aluminum Satisfactory to Resist Ammonium Nitrate Corrosion*

AMMONIUM NITRATE production in a fertilizer plant has caused serious corrosion problems. Because this chemical readily absorbs moisture, nitric acid can be liberated as the wet ammonium nitrate slowly decomposes.

For this reason, steel should be eliminated in the design of an ammonium nitrate plant except for uses where the steel is kept hot enough to avoid deposition of moisture which would promote corrosion. Where steel is used as heavy structural members, for example, adequate protective measures must be taken by coating with an epoxy or other materials resistant to ammonium nitrate attack.

Aluminum has been suitable for use as light structural members, roofing and siding in areas subjected to ammonium nitrate. However, special precautions must be taken to provide electrical insulation between the steel and aluminum to prevent galvanic corrosion between dissimilar metals.

Ammonium nitrate also will attack concrete, causing the crystal structure to disintegrate, the calcium to become soluble and the concrete to lose its strength completely. Thus, concrete must be protected by special surfaces such as acid resistant brick or troweled epoxies.

Localized corrosion attacks on steel and concrete can be prevented by eliminating crevices and corners when the plant is designed so that ammonium nitrate dust will not accumulate. (See Henry T. Rudolf's article "Design Against Atmospheric Corrosion" published on Page 347t of the August, 1955, issue of CORROSION.)

Despite aluminum's high corrosion resistance to ammonium nitrate, serious problems can occur. For example, if the ammonium nitrate contains a small amount of acid, aluminum (especially its alloys) may be attacked by the acid. Frequently this attack will be seen first in the area of a weld where a different alloy welding rod was used.

Because aluminum is attacked by ammonium nitrate solutions above 90 percent concentration, stainless steel is used for this strong solution service.

Use of large stainless steel tanks for storage of ammonium nitrate solutions was deemed prohibitive at the fertilizer plant because of cost. The plant stored as much as three months' production, making the cost too high for stainless steel storage tanks.

To solve this problem, it was determined that aluminum would be satisfactory for strong solution storage if the solution's pH were maintained above the 5.0 level, accomplished by addition of ammonia. Storage tanks are checked daily to be certain the correct pH conditions are maintained.

Contamination of some tank plates with mercury is determined to be the cause of corrosion in specific areas of the tank. Mercury forms an amalgam with aluminum which in turn is broken by the oxidation of the aluminum, leaving the mercury to return to the metal surface to amalgamate again with a fresh quantity of aluminum.

After the first corrosion on specific plates of these storage tanks, there has been a gradual spreading of corrosion despite efforts to remove all corrosion products from the tanks. The corrosion rate has been reduced but is not under complete control.

★ Extracted from a paper titled "Corrosion Considerations in a Fertilizer Nitrogen Chemical Plant" by Robert T. Lukat, Southern Nitrogen Company, Inc., Savannah, Ga., presented at the Southeast Region Conference, National Association of Corrosion Engineers, October 6-8, 1960, Atlanta, Ga.

Technical Topics Included in Index

Technical Topics will be included in CORROSION's annual index published in the December issue. The Topics will be cross-referenced in the alphabetical subject and author index.

Persons who customarily extract Technical Section pages from each issue for binding are reminded that the Technical Topics pages should be extracted also for a more complete reference to technical information published in CORROSION.

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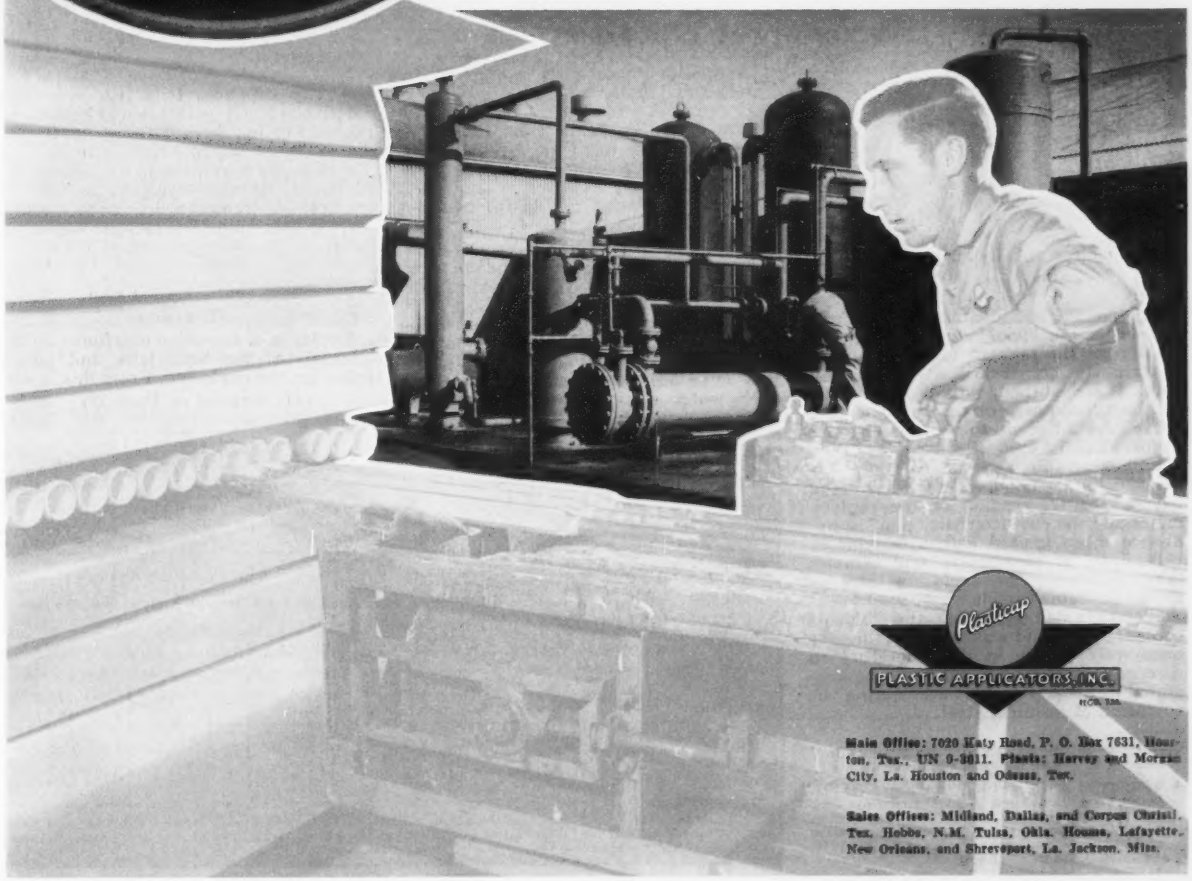

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Corrosion-Generated Hydrogen Explodes in Phosphoric Acid Tank*

J. B. Lowe
Port Hope, Ontario, Canada
Eldorado Mining and Refining Ltd.

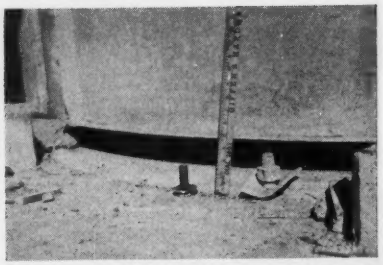

Figure 2—Explosion dished the tank bottom. Top of tank also was dished about six inches at highest point.

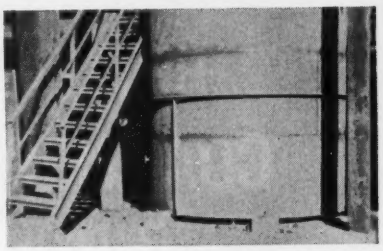

Figure 3—Superstructure and staircase on tank were bent by explosion.

Abstract

An investigation of an explosive reaction in a stainless steel tank storing 75 percent phosphoric acid showed hydrogen gas probably was ignited by electrical level control. Unexpected generation of gas by corrosion of Type 304 stainless steel was confirmed by laboratory tests in which known amounts of chloride were added to reagent grade phosphoric acid. 1.2.5

AT 11:30 a.m. on August 16, 1959, a violent gaseous reaction of explosive magnitude occurred in a verticle, cylindrical stainless steel tank holding 75 percent phosphoric acid at Port Hope. Ontario, Canada. Considerable damage was done to the surrounding structural members as well as to the tank itself. This report summarizes results of an investigation conducted by the Refining Division of Eldorado Mining and Refining, Ltd., to determine the cause of the explosion so that measures could be taken to prevent similar explosions.

Mechanics of the System

Phosphoric acid is pumped from a storage tank to a head tank and from there distributed by gravity flow to the point of requirement. (See Figure 1.) The level in the upper tank is maintained within a prescribed range by electrical level probes which automatically energize the distribution pump. The head tank is vented through an overflow line to the storage tank which in turn has a 1½-inch vent open to the atmosphere.

The storage tank holds 3100 gallons and is made of Type 316 stainless steel. The head tank, located about 30 feet above the storage tank, has a volume of 160 gallons and is made of Type 304 stainless. The distribution pump is made of a low carbon anstenitic stainless steel[1] and the inter-connecting piping is Type 304 stainless with welded joints.

Incident and Related Details

An eye witness heard pressure escaping from around the manhole cover and the flange on the filling nozzle. This was followed by a "poof" which raised the flat top of the tank to form a dish approximately six inches at its highest point. It dished the tank bottom similarly and bent the superstructure and staircase above and adjacent to the vessel. (See Figures 2 and 3.)

Following this, an examination of the gas-air mixture taken from the head tank gave a positive reading on the explosimeter and the characteristic "pop" of hydrogen when ignited with a match.

Analysis of phosphoric acid samples taken following the explosion were as shown in Table 1.

It was noted also that the chloride content of the acid was unusually high so tests were set up in the laboratory to determine if hydrogen gas could be generated in quanity by this acid during the corrosion of stainless steel.

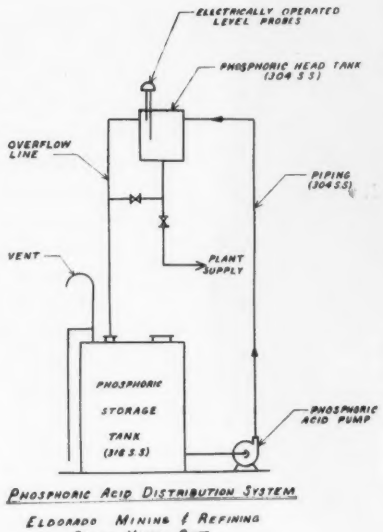

Figure 1—Flow diagram of phosphoric acid distribution system.

Results of these tests are given in Tables 2 and 3.

The corrosion rates based on plant acid results shown in Table 2 for 168 hours were 0.00014 ipy for Type 316 and 0.221 ipy for Type 304.

Tests Simulating Head Tank Environment

Phosphoric acid (75 percent) for the tests was prepared by diluting 85 percent phosphoric meeting ACS specifications (less than 5 ppm Cl) and adding to it known amounts of chloride. These solutions then were placed in flasks containing test pieces (¾ x ¾ x ⅛-inch) of stainless Type 304, stoppered and connected with water displacement apparatus to trap any off-gases from the corrosion reaction. The temperature was held in the range of 85 to 100 F to approximate conditions in the phosphoric acid head tank. The reaction was allowed to proceed for 60 hours. Results tabulated in Table 3 are noteworthy in that it is not generally known that chlorides in H_3PO_4 greatly accelerate the corrosion of 18-8 stainless steels, especially those which do not contain molybdenum.

Discussion

Evidence of corrosion was found on the internals of the head tank and piping following the explosion. From this, it was

(Continued on Page 32)

TABLE 1—Analysis of Phosphoric Acid Samples

Location	Percent H_3PO_4	PARTS PER MILLION						Reduction of $KMnO_4$
		Cl	Fe	Ni	Cr	SO_4	NO_3	
Storage Tank	74.84	334	43	2	1	250	1	(1)
Head Tank	74.90	356	646	3	2	250	9	(1)

(1) Meets ACS specifications.

TABLE 2—Tests for Hydrogen Generation

S.S. Type	Acid[1]	Original Wt. Gms.	Wt. after 48 Hours	Wt. after 120 Hours	Wt. after 168 Hours
316	Reagent	15.6928	15.6920	15.6916	15.6918
316	Plant	15.6853	15.6795	15.6764	15.6586
304	Reagent	15.8702	15.8692	15.8692	15.8696
304	Plant	15.8631	15.5938	15.1193	11.7334

[1] The plant acid used in the test was from the head tank with analysis shown in Table 1. Test was conducted at room temperature without aeration or agitation. Reagent acid was 85 percent H_3PO_4, meeting ACS specifications.

(1) Durimet 20: Nl 29; Cr 20; Mo 2 min; Cu 3 min; Sl 1; C 0.07 max and balance Fe.

★ Revision of a paper titled "An Explosive Reaction in a Phosphoric Acid Distribution System" presented at the Eastern Division Conference, Canadian Region, National Association of Corrosion Engineers, January 17-20, 1960, Toronto, Canada.

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TABLE 3—Corrosion of Stainless Types 304 & 316 by Phosphoric Acid Containing Known Amounts of Chloride

Alloy	Test Piece Number	PPM Cl Added	WT. OF TEST PIECES Before	WT. OF TEST PIECES After	Wt. Loss In Gms.	Percent Wt. Loss	H_3PO_4 Color	Off Gases	Approx. ipy
304	1	0	10.0973	10.0977	Nil	Nil	Clear	None	.....
304	2	8	10.0787	10.0780	0.0007	0.007	Clear	None	0.00137
304	3	15	10.2907	10.2852	0.0055	0.05	Clear	None	0.0108
304	4	23	10.9738	10.7142	0.2596	2.36	Green	H_2	0.508
304	5	39	10.5246	10.0600	0.4646	4.41	Green	H_2	0.910
304	6	117	9.5149	9.0179	0.4970	5.22	Green	H_2	0.973
304	7	156	10.2755	9.8119	0.4636	4.51	Green	H_2	0.903
304	8	196	10.6438	10.1417	0.5121	4.81	Green	H_2	1.081
304	9	274	10.7473	10.3732	0.3741	3.48	Green	H_2	0.733
304	10	391	9.2585	8.7932	0.4653	5.03	Green	H_2	0.912
316	11	196	15.2468	15.2465	0.0003	0.002	Clear	None	0.0006

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Tel. Circle 5-1351

Phosphoric Acid Tank—

(Continued From Page 30)

assumed that a reaction took place similar to the one noted below.

$(3\ Fe + 2H_3PO_4\ FE_3(PO_4)_2 + 3H^2)$ or

(56 gms. Fe produce 2 gms H^2) and

(2 gms H^2 at NTP = 0.79 ft^3)

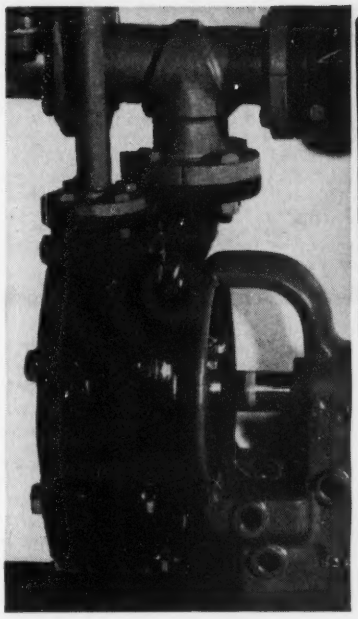
The probe system uses the electrical conductivity of the phosphoric acid with the tank forming part of the electrical sensing circuit (ground). A high voltage current normally flows between the vessel wall and the probes when they are covered with acid. Conceivably it could produce a spark when contact is made or broken during level fluctuations.

Conclusions

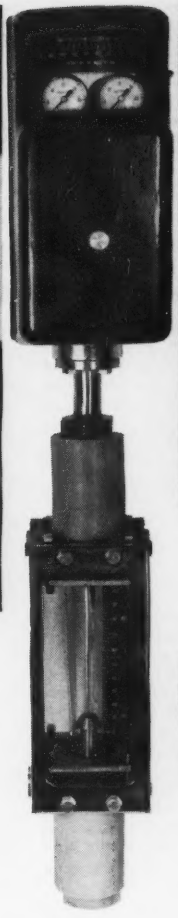
1. The explosive reaction in the phosphoric distribution system appears to have been caused by the ignition of hydrogen.
2. Hydrogen gas is produced rapidly when phosphoric acid contaminated with chloride corrodes Type 304 stainless steel.
3. Ignition of the gas appears to have been triggered by the electrical level probe causing the reaction $2H^2 + O^2 2H_2O$ + heat to take place.
4. Eldorado will not store or handle phosphoric acid containing 15 ppm or more chloride in Type 304 stainless steel tanks or pipes.
5. Hydrogen in the Type 316 ss storage tank probably was generated in the Type 304 head tank and displaced by the H_3PO_4 via the overflow line.

Technical Topics On Coatings Scheduled For Future Issues

Effect of Some Application Variables on Maintenance Coating Performance, by J. R. Allen, F. W. Thompson and M. L. Monack
Laboratory Tests for Rapid Evaluation of Ship Bottom Coatings, by J. R. Brown
Epoxies Give Good Service in Well Casing Coating Test, by W. R. Lambert
Evaluation of Some Materials and Coatings for Utility Pole Line Hardware, by John S. Melvin
Susceptibility of Epoxy Coatings to Damage by Fresh Water Immersion, by Harold Moroson
Responsibilities of High Performance Maintenance Coating Manufacturer, by C. G. Munger
Special Coupon Shapes Used in Testing Liner Coatings, by O. W. Siebert
Practical Data Concerning Baked Phenolic Coatings Used in Process Industries, by L. S. VanDelinder



This pump has a 25 mil Penton coating applied by fluidized bed process to pump impeller and both the inside and outside of pump head, providing internal protection against corrosive fluids as well as an exterior surface finish resistant to corrosive atmosphere.
(PHOTO COURTESY GOULDS PUMPS, INC.)



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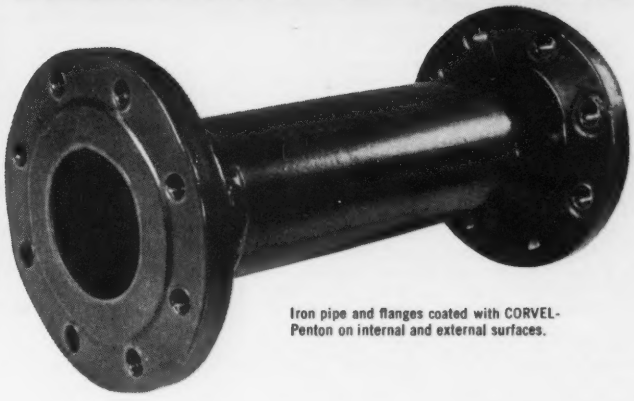

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Effects of Alternating Currents In Causing Corrosion*

F. E. Kulman

Consolidated Edison Company of New York, Inc.
New York, New York

Brief Historical Review

In 1907, Hayden[1] reporting on tests on lead electrodes in soil showed that the corrosive effect of small a-c currents was less than 0.5 percent compared with the effects of equal d-c currents.

McCollum and Ahlborn[2] described experimental work to determine the rate of corrosion of iron and lead electrodes buried in soil and subjected to a current density of about three milliamperes per square inch. They were interested in the effect of frequency of reversal of the current and found that corrosion decreased as the frequency increased from one cycle in a two-week period to 60 cycles per second.

S. Marsh[3] presented a study of the electrode reactions occurring upon a-c electrolysis of platinum, gold and nickel electrodes in sulfuric acid and barium hydrate solutions at frequencies of 25-80 cycles.

E. R. Shepard[4] made investigations to corroborate several of the conclusions of McCollum and Ahlborn in respect to corrosion by direct current and infrequently reversing currents. However, no tests were made at frequencies in the order of 25 to 60 cycles per second.

K. W. Miller[5] discussed means of reducing corrosion caused by induced a-c sheath currents, and voltages on lead sheathed single conductor cables installed underground, and suggested that 10 volts, a-c voltage, on the sheath could produce electrolysis equivalent to an anodic voltage of about 0.5 volt d-c.

Searing and Kirke[6] reporting on an investigation of cable lead sheath corrosion at 60 cycles per second, stated that the metal loss per unit current density of one milliampere per square inch was about 2.7 mils per year for underground cable.

Shipley[7] in Canada reported on experiments in water heaters energized by 60-cycle current flowing between immersed electrodes. With iron electrodes, the fresh water was electrolyzed when the current density exceeded a critical value of 2.5 amperes per square centimeter. The critical current for copper was 1.9 amperes per square centimeter. The generation of hydrogen and oxygen gases was accompanied by corrosion of the electrodes, but no weight losses were recorded.

Shipley and Rogers[8] investigated the chemical oxidation and reduction of organic compounds by 60-cycle current and found that electrodes of commercial metals were unsuitable as they were severely corroded by the a-c current and, furthermore the corrosion products interfered with the electrolysis of the solutions.

Sherer and Granbois[9] investigated the corrosion of underground lead sheath cables by constructing lead-copper cells with alkaline duct water as electrolyte. When 25-cycle current was impressed, the d-c current flowing from the clean lead anode to the electrolyte was increased. However, in tests with old (corroded) electrodes, the lead was cathodic and became more cathodic as larger a-c currents were applied. (Thus it would appear that a lead cable traversing unaerated and aerated environments might be corroded in both environments by induced a-c currents, since the effects could be cumulative.) Field tests on operating cables, in which the induced sheath voltage varied linearly with the load current, showed that increases in the a-c load resulted in net increased cathodic currents flowing to the lead sheath.

Silverman and Rennick[10] made fundamental studies of alternating current electrolysis using platinum electrodes in ferrous sulfate solution and ferric sulfate solution. Oscillograph traces were obtained of the cyclic variations of instantaneous potential difference and current flow between the electrodes. Interpretation of the traces showed that during each cycle, there were regions of polarization, oxidation of the ferrous ions to the ferric state, reduction of ferric ion to the ferrous state and reduction of the hydrogen ions.

Bellassai[11] made measurements of a-c voltage on a coated gas pipeline which had undergone corrosion in a swampy soil. The pipe voltage was 8.5 volts at 60 cycles. Soil resistivity was 76 ohm-centimeter. Tests to determine the presence of a rectified current were inconclusive and it was decided that the corrosion was caused by concentration cell action.

Darratt[12] showed that gas pipelines paralleling a high voltage electric tower line were subject to inductive effects. Under normal operating conditions, induced voltages as high as 10 volts per mile could be measured.

Woodward[13] discussed corrosion of telephone cables installed in underground ducts close to a railroad operating at 25 cycles, alternating current, and postulated that direct current flowing in the telephone cable sheath may have been the result of rectification of a-c leakage current from the railroad tracks.

Haring[14] discussed the mechanism of electrolytic rectification and presented a theory for aluminum and tantalum electrodes. These form oxide films which are characterized by an excess of metal ions (aluminum and tantalum). With aluminum or tantalum, the film blocked the flow of current whenever the electrode was anode. The film passed current (electrons) when the electrode was cathode. With alternating voltage applied, a rectification process occurred in which the rectified current flowed from the electrolyte to the aluminum.

The results of a survey of gas companies represented on the A.G.A. Corrosion Committee in 1955 showed that 27 companies had experienced induced a-c voltages on their pipelines. Seven had suspected that a-c current had been the cause of pipe corrosion.[15]

In 1957, Amy and Mounios[16] made tests with lead and iron electrodes immersed in calcium sulfate solution. When 50 cycle a-c voltage was impressed, the a-c current was 200 milliamperes and there was a 10-fold increase in d-c current to 0.7 milliampere. The direction of d-c current flow was from the lead through the electrolyte to the iron. When alternating voltage was applied to two identical electrodes of lead in calcium sulfate solutions both electrodes were corroded.

In the same year, R. Bentley and T. R. Prentice[17] presented a paper on the mechanism and frequency dependence of corrosion of stainless steel, platinum and gold electrodes passing a-c current in acid solutions.

Probably the broadest investigation of a-c electrolysis of iron electrodes in salt solutions was made by Fuchs, Steinrath and Ternes.[18] They made tests on steel electrodes subjected to current densities of 10, 100 and 1,000 milliamperes per square decimeter, at frequencies ranging from 0.05 to 50 cycles per second, and in sodium chloride and sodium sulfate electrolytes. Translating their results into practical applications, it can be deduced, for example, that a combination of a-c voltage on the coated pipeline and low soil resistivity which would result in a leakage current density of 10 milliamperes per square centimeter area would cause a-c electrolysis at the rate of 0.010 inch per year. A specific set of conditions which would result in this corrosion rate would be 10 volts (a-c), soil resistivity of 1,000 ohm-centimeters, and a one-inch diameter break in the coating. This would assume the absence of rectifying films elsewhere on the pipe or on metallic attachments to the pipeline which would complicate the condition.

G. Mole and D. P. Hammond[19] found no evidence of any increased tendency to corrosion of a buried water system as the result of stray alternating current originating from the electrical transmission system. Specifically, an a-c current density of 0.25 milliampere per square centimeter failed to change the d-c pipe potential referred to earth.

Bruckner and Jansson, working in Illinois[20] presented results of laboratory tests on cathodic protection of lead sheaths. A significant factor in the test was the use of non-symmetrical electrodes which resulted in corrosion because of non-uniform current densities.

Rectified Current as a Factor in Corrosion

As shown by previous investigators, electrolytic corrosion can occur on identical electrodes without manifestation of a uni-directional current. However, a direct measurement of the rectified current component, if present, could give a clue as to the probable rate of corrosion. The magnitude and polarity of the current are both important. Anodic currents would, of course, be of most direct concern. However, cathodic currents also would be of interest because of their indirect corrosive effect on neighboring structures which would become anodic. The "neighboring structure" could conceivably be a portion of the same gas pipeline exposed to an alternating field. The following information on polarity was obtained from the brief preliminary search of the literature.

★ A paper presented at the 1960 American Gas Association Operating Section Distribution Conference.

Amy and Mounios[16] found lead to become more anodic with respect to iron when alternating current was applied and measured a d-c component of current.

Haring's work[14] shows that aluminum and tantalum become more cathodic when alternating current is applied. (Aluminum corrodes under cathodic conditions.)

Shipley[7] did not measure the current flow in water solutions, but found that the presence of an oxide film on copper prevented the electrolytic decomposition of water caused by alternating current.

Composition and Fluidity of the Electrolyte

The chemical composition of the electrolyte has been found to have an effect on corrosion and on the films formed on metal. The films formed may be very important in causing rectification. Whether a film forms on a metal depends in part on the chemical composition and oxygen content of the soil electrolyte.

Solutions of sodium chloride were used by Fuchs, Steinrath and Ternes.[18] Sulfate solutions also were used by these investigators and by Amy and Mounios.[16] Fresh water was used by Shipley.[7] Sherer and Granbois[9] used alkaline water from underground cable ducts.

McCollum and Ahlborn,[2] who tested lead and iron electrodes buried in soil, and in soil containing added carbonate, concluded that the extent to which the a-c corrosion process is reversible depended upon the freedom with which the electrolyte circulates. Thus, metals exposed to soils would undergo more rapid a-c electrolysis than metals exposed to solutions. Sherer and Granbois[9] placed porous cups over the electrodes "to keep the corrosion products near the corroding surfaces, thus simulating conditions of the cables in the ducts."

Size of Electrode and Effect of Current Density

The size of the metal electrode determines the current density, other factors being unchanged. The density of current would be much higher at a small coating break on a steel pipe than on bare pipe, for example; thus with coated pipe, the problem of a-c electrolysis would probably assume greater significance than with bare pipe.

The size of the electrode and the factor of current density appear to have been neglected by many of the previous investigators. However, several investigators appear to have considered the current density important. Searing and Kirke[6] measured current density on lead electrodes, and McCollum and Ahlborn[2] on lead and iron electrodes. Fuchs, Steinrath and Ternes[18] made tests at various levels of current density and took size of the steel electrode into account.

Non-Symmetrical Electrodes

The arrangement of buried pipes and cables is far from symmetrical. In congested areas, occupied by several utilities, there are found various sizes of pipes and composed of different metals, e.g. steel, cast iron, copper, lead and aluminum. Many of these pipes are interconnected electrically and some may be cathodically protected.

To represent the actual piping situation by a laboratory model of an electrolytic cell in which the electrodes are of identical size and of the same material may be an over-simplification, and conclusions from experiments on such a model should be made with considerable reservation. Variation of the size and shape of the electrodes would serve to provide more information on the effects of varying current density. In this respect, Bruckner and Jansson[20] using non-symmetrical electrodes obtained corrosion rates previously unobtainable with more simple configurations.

The contribution of dissimilar metals to the rectification process is not well known. It is possible that galvanic cells caused by use of dissimilar metals assist in the formation and maintenance of rectification films. These rectifying films may cause an increased anodic or cathodic current to flow when a-c potential is applied, depending on the polarity of the rectified current.

Status of the Problem (1960)

There is no question that alternating currents have caused electrolysis. This is not the question confronting the corrosion engineer. The problem of interest and importance rather is *under what conditions* can a-c electrolysis occur or be prevented from occurring.

Many of the early and some of the later laboratory investigations were conducted with current densities in the order of one-twentieth of the magnitude of present-day current densities. This is particularly true of the oft-quoted Bureau of Standards work by McCollum and Ahlborn[2] and the British work including a study[19] made in 1958.

For a given a-c voltage on the pipe, the current density at the pipe-soil interface may be much greater at breaks in coatings than on a completely bare pipe. This results from the concentrating effect of coating breaks.

The incidence of a-c corrosion of pipelines is expected to increase in the future as available right-of-way space becomes scarce in the vicinity of generating stations, and as gas lines are laid closer to overhead electric lines.

Aluminum appears to be more susceptible to a-c corrosion than ferrous materials. As aluminum pipelines and gas meters are installed, the risk of a-c corrosion will be expected to increase.

There is no evidence that studies are being made on the problem of a-c corrosion in the United States. The last significant contribution seems to have been made by Sherer and Granbois working on lead electrodes in 1945.

In Italy, Dr. R. Piontelli has been studying the a-c corrosion of iron, nickel, copper, aluminum, zinc, tin and lead. The following aspects are being investigated:

1. Effect of current density and frequency
2. Effect of electrolyte and environment
3. Effect of structure and surface condition of the metal

The subject of a-c corrosion is quite complicated and will require a large amount of systematic work to achieve any definite results. For this reason and the slow progress he is making because of meager financial support, Dr. Piontelli does not feel that any substantial duplication of effort will occur if other research centers undertake work along the same lines.[21]

Until the results of laboratory research investigations are received the corrosion engineer concerned with underground plant will not be able to evaluate the degree of existing corrosion hazards caused by a-c voltages and currents on metal structures or equipment in contact with the earth.

Abstract

Corrosion of buried or submerged metals is an electrochemical phenomenon in which direct currents usually are associated. However, reversing and alternating currents can cause corrosion, although at a lower rate than direct currents.

A brief review of the technical literature shows that numerous investigations have been made having a bearing on a-c electrolytic corrosion of iron, lead, copper, aluminum and other metals. These investigations have been concerned with such diverse ends as decomposition of water into hydrogen and oxygen, reduction of organic compounds, ascertaining the cause of pitting and corrosion in buried structures, reducing the shock hazard on pipelines due to induced voltages, determining the allowable levels of a-c voltage induced in cable sheaths, as well as attempting to determine under what conditions a-c electrolytic corrosion occurs, and the mechanism of rectification at the oxide film surfaces of metals.

No single investigation has been sufficiently comprehensive to permit a prediction as to what corrosion rate will result on buried structures. Taken together, however, the investigations suggest that a-c electrolysis is a complex phenomenon which depends on various factors, all of which probably exert influence on the rate of corrosion. 3.8.2

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18. "Corrosion of Iron by Alternating Current with Relation to Current Density and Frequency," Walter Fuchs, Heinrich Steinrath, and Helmuth Ternes. *Das Gas-Und Wasserfach*, Vol. 99, (1958) January, Pages 26-9, 78-81.
19. "Does Stray Alternating Current Corrode Water Systems?—Investigation of Installation at Rockdale," G. Mole and D. P. Hammond, Technical Report V/T 138 of The British Electrical and Allied Industries Research Association (1958).
20. "Cathodic Protection of Lead Cable Sheath," W. H. Bruckner and Ole G. Jansson, *Corrosion*, Vol. 15, (1959 Pages) 67-72.
21. C. G. Wilson letter of September 17, 1959 to F. E. Kulman.

NEW! SPRAY FLOOR COATINGS 5 TIMES FASTER THAN TROWEL ...CUT LABOR COSTS 75%

Heavy thickness floor coatings can be sprayed on with Carboline's new Floor Spray Gun. Ten gallon capacity covers 140-160 sq. ft. at 3/32" thick in 10-12 minutes. Averages 2500 sq. ft. per day (vs. 500 sq. ft. with trowel). Application costs 5¢ per sq. ft. (vs. 20¢ with trowel). Produces smooth, even surface; no trowel ridges. Easily covers corners, vertical surfaces. Use Carboline's Floor Spray Gun on your next job!

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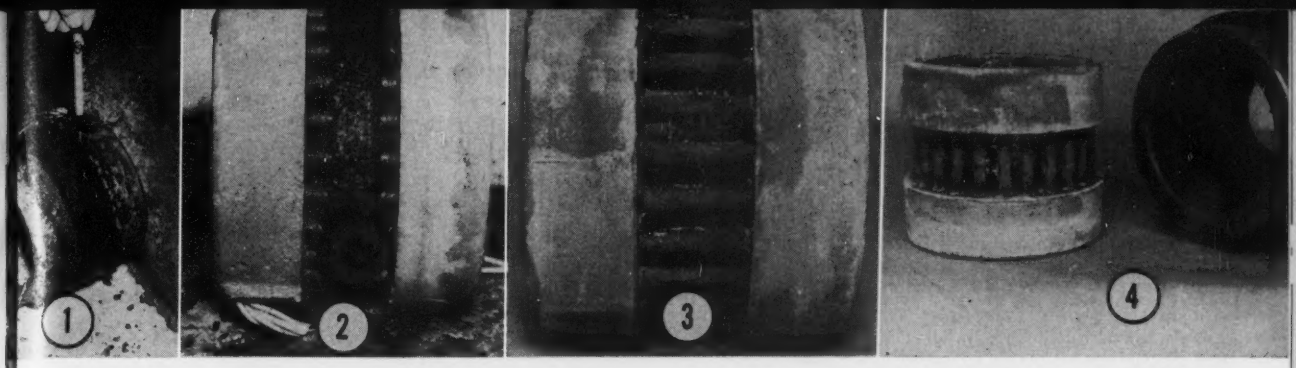
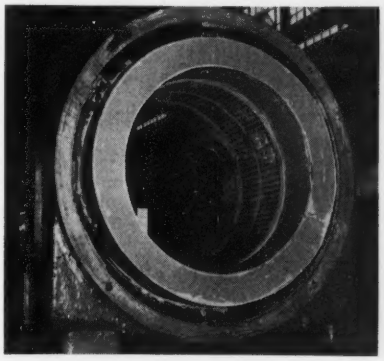
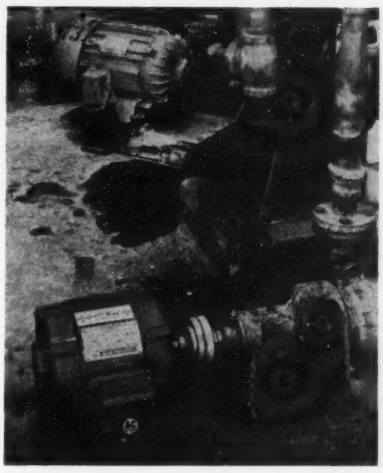


ACID TEST shows corrosion resistance of the epoxy resin encapsulation on the electric motor stators. Acid used as 52.3 percent nitric. Photograph 1 shows the stator after 8 days, Photograph 2, 18 days, Photograph 3, 23 days and Photograph 4 compares an unexposed stator with the one exposed for 23 days. The acid progressively destroyed the metallic components of the stator, leaving the encapsulating resin intact. (Allis-Chalmers Mfg. Co. photographs)



EPOXY RESIN encapsulation was cast for the 75 hp motor for service in caustic environment. This motor was encapsulated during rewind. (Photograph from Larsen-Hogue Electric)



CONDENSATE PUMPS handling orange rind molasses at a Florida frozen juice plant. The Allis-Chalmers motor in the foreground has Poxeal insulation, another type of epoxy resin encapsulation. Encapsulated motors are specified for this service in place of TEFC motors, one of which is shown in the background, giving a comparison of size between the two types of motors.

Encapsulation With Epoxy Resin Protects Electric Motor Stators

Electric motor stators have been encapsulated with epoxy resin for protection from moisture, salt spray, steam and contaminants that can cause corrosion with resultant motor failure.

The epoxy encapsulation system is proving to be a more satisfactory and less expensive method of protecting the stators than other methods such as the TEFC type motor (totally enclosed, fan cooled).

Epoxy encapsulation is designed to protect the most vulnerable part of the motor against corrosive attack. About 25 to 30 percent of electric motors used in industry are exposed to corrosive environments ranging from mild to extreme. Exposures can range from salt water spray on offshore drilling rigs and steam, caustic and brine in a meat processing plant to sulfuric acid, lye and hydrochloric acid in a chemical processing plant.

Encapsulation Process Described

Corrosion engineers are familiar with the characteristics of epoxy resins as industrial protective coatings for severe environments. Unlike these coatings, however, resins for encapsulating motors contain no solvents and are applied in thicknesses several hundred times that of conventional solution coatings to provide increased corrosion protection over that obtained by films.

The encapsulation process consists of filling all interstices and encasing motor windings in a sheath of epoxy resin as shown in accompanying photographs. This is accomplished by pouring a fluid resin over the windings and then allowing this to cure. Molds are used to retain the resin and to control the build-up.

The main problem in obtaining an epoxy resin to protect large electrical equipment is one of thermal shock. Under the worst conditions of service, for example, a motor operating at 130 C might be sprayed with ice cold water during a cleaning operation. All motor components—iron, copper, various insulating materials and the encapsulating epoxy—rapidly change dimensions at different rates, setting up stresses within the encasing resin. Should these stresses crack the resin, corrosive elements can enter to attack the vulnerable windings and quickly destroy the motor.

Thermal shock tests have been made to develop motor encapsulating resins. A typical resin is Epoxylite, trade mark of the Epoxylite Corporation of South El Monte, California. Motors protected with this material have been frozen solid and started under full current. As the current melts the ice, unlocking the motor, the melting ice cannot short the motor because the windings are encased in epoxy. Other tests included placing motors in dry ice boxes at —40 F before cycling them repeatedly through the operating ranges.

Problem of Voids in Epoxy

Another problem was development of an application technique which would permit full-scale production and assure void-free castings of the epoxy around and through the windings of the motor.

If voids occur within the epoxy casting, they will act as heat-traps and will cause thermal rises above the motor's temperature rating.

Advantages of Encapsulated Motors

In addition to the corrosion resistance of the epoxy encapsulation, a motor protected with this system has the advantage of cost. On new equipment, an encapsulated motor in most sizes is priced about midway between the price of drip-proof and TEFC motors. Price for an encapsulated rewound motor compared with a standard rewind is usually greater than for a new encapsulated motor compared with a new standard motor. This is because of the labor required to construct individual molds for encapsulating a rewound motor.

Another advantage of the epoxy protected motor is its weight. The encapsulated motor often is less bulky and weighs less than a TEFC motor of similar design, as illustrated in the accompanying photographs.

(Continued on Page 38)

NACE Helps With Specifications For Surface Preparation of Fans

A recommended practice for surface preparation of fans and fan parts has been prepared by the Air Moving and Conditioning Association in cooperation with NACE. Arno J. Liebman, NACE member with Pitmar Corporation, 1000 West Ave., Rochester, N. Y., worked with AMCA in preparing the recommendations. The practice has been designated AP 2601, Sept. 7, 1960.

The recommended practice suggests steps or procedures to make protective coatings on fans more effective in preventing corrosion when they are exposed to corrosive fumes or atmospheres.

Preparation of fans for protective coatings is suggested in two ways: (1) design considerations to eliminate sharp edges and configurations which are not easily coated and (2) surface preparation of the metal surface to remove grease or scale that might prevent proper bonding of the coating to the fan.

Design considerations include replacing bolts normally threaded into the coated surface with studs or bolts having heads continuously welded inside. Self-tapping screws and permanent threads protruding into the coated surface should be eliminated. Hairline cracks and sharp inside corners should be eliminated by continuously welding, brazing or filling with high melting point solder. Because bearings cannot be adequately protected, it is suggested that they be placed outside the airstream.

Welds should be peened or ground reasonably smooth and outside corners ground to about 1/16-inch radius on all surfaces to be coated.

Suggested surface preparation methods include the following: Wire brushing, chipping, discing, sandblasting and chemical cleaning by solvents, acids and alkalis. Steam cleaning also is recommended.

More German Standards Published in English

German standards published in English for November, 1960, include the following items of probable interest to corrosion engineers:

UDC 621.643.2 Pipes, Conduits: 1754 Copper tube, seamless drawn, dimensions (March, 1960); 8061 Tube and piping of rigid PVC, technical delivery specifications (preliminary standard, July, 1960); 8062 Tube and piping, dimensions (July, 1960); 8072 Tube and piping, flexible polyethylene, dimensions (July, 1960); 8073 Tube and piping, technical delivery specifications (July, 1960); 8074 Tube and Piping, rigid polyethylene, dimensions (July, 1960); 8075 Tube and piping, technical delivery specifications (July, 1960).

DIN UDC 669.2/.8-4 Half-finished products: 9715 Magnesium wrought alloy semi-products, mechanical properties (April, 1960).

UDC 669.2/.8 Non-ferrous metals: 1620 Mild steel, rolled; sheets and plates, general specifications (March, 1958); 1729 Sheet 2 Magnesium alloys; cast alloys, sand castings, permanent mould casting, die castings (April, 1960).

These standards are available from Deutscher Normenausschuss, Uhlandstrasse 175, Berlin W 15.

Electron Beam Technology Meeting to Be March 23-24

The Third Annual Symposium on Electron Beam Technology will be held March 23-24 in Boston. Sponsored by the Alloyd Electronics Corporation, the symposium will have sessions on electron beam physics, welding and refining, advanced techniques such as polymerization, food processing and other areas. Additional information can be obtained by writing R. Bakish, 37 Cambridge Parkway, Cambridge 42, Mass.

Canada's First Detinning Plant Under Construction

Construction has begun on Canada's first detinning plant at Hamilton, Ont., where Metal & Thermit Corporation is building a new plant to remove tin from high quality scrap produced in can making operations. Tin chemical by-products will be a source of sodium and potassium stannate used in electroplating with tin and for immersion coating of aluminum pistons for internal combustion engines.

The company is a subsidiary of Metal & Thermit Corporation, Rahway, N. J. The company has other detinning plants in operation at Carteret, East Chicago, South San Francisco, Los Angeles, Baltimore, and Tampa, Fla.

Electric Motor Stators—

(Continued From Page 37)

Case History of Motor Protection

A case history illustrates the protection which can be obtained by epoxy encapsulating a motor.

Average life of a TEFC motor driving a centrifuge basket for lithium mixed sulfate was three months. An encapsulated motor installed as replacement in the same service has been in service for six years.

The Epoxylite Corporation and its franchised motor repair shops report that about 25 percent of the motors rewound by them have been TEFC types that had failed because of environmental extremes. One motor's enclosure was one-quarter full of water. These motors were examples in which moisture and corrosive vapors had been sucked into the motors through the system of seals.

Limitations of Encapsulated Motor

At the present, encapsulating is limited to the small industrial motors. The larger, random wound, higher temperature motors have severe thermal shock requiring special epoxy resin formulations which would be expensive and not readily adaptable to production operations.

Commercially available encapsulated motors are not suitable for some environments involving submersion and extremely corrosive elements such as submerged gasoline pump motors and motors for Freon service. Epoxy resin systems capable of protecting motors for these services require special designation when ordering.

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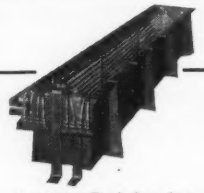

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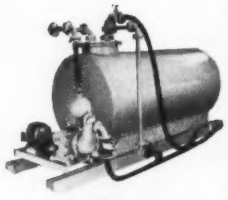

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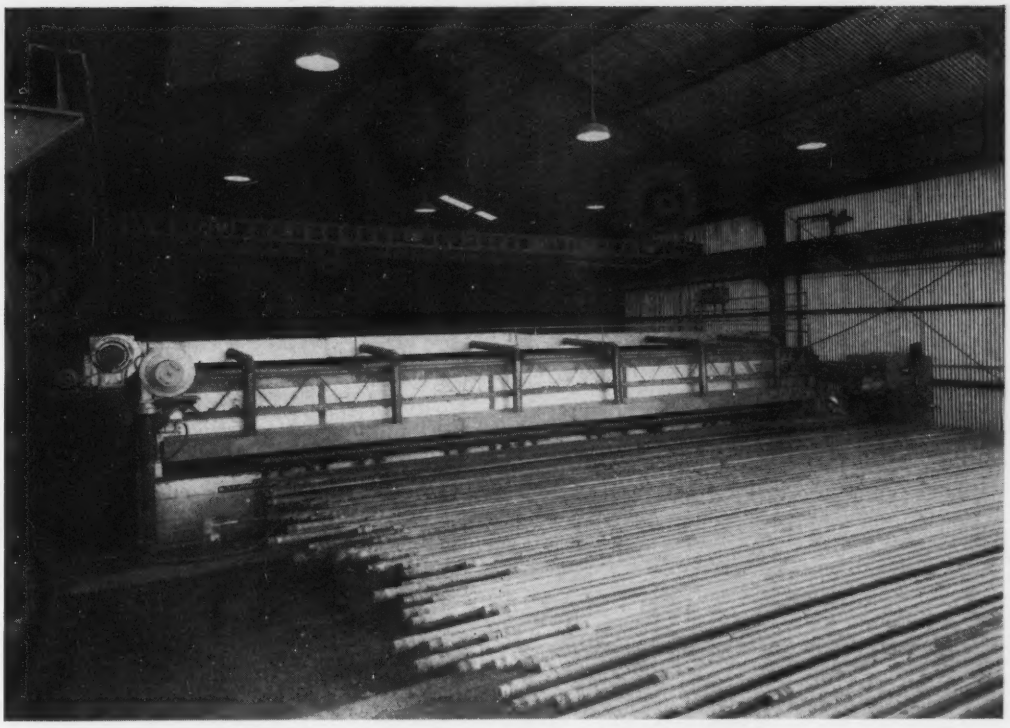

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Tubular Lining Corporation now brings to plastic lining users the "Thermo-Pickled" method—the TLC exclusive automatic metal cleaning process. Internal surfaces of tubing are cleaned to a new degree of refinement—free of foreign matter and neutral in pH. After arrival at TLC, tubing is inspected, enters the automatic "Thermo-Pickled" processing machine, is automatically sandblasted and re-inspected. Approved tubing then enters the automatic "Autotronics" lining equipment that applies and bakes coats in controlled succession by an endless process to give a flawless lining that resists corrosion and paraffin deposits. At TLC, uniform bake cycles assure positive bond and cure.

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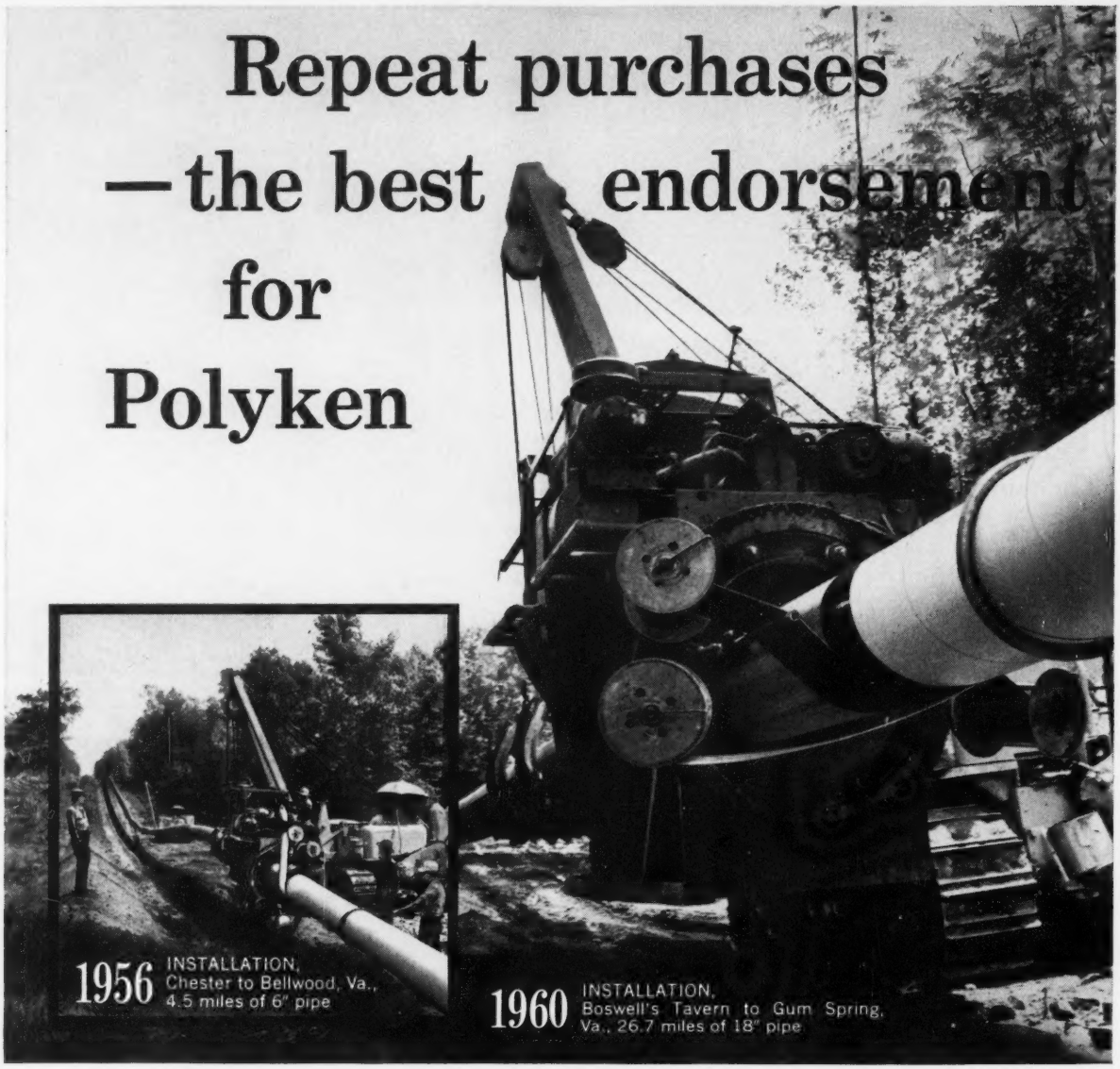
1956 INSTALLATION, Chester to Bellwood, Va., 4.5 miles of 6" pipe
1960 INSTALLATION, Boswell's Tavern to Gum Spring, Va., 26.7 miles of 18" pipe

Commonwealth Natural Gas makes repeated use of Polyken® tape on strength of past performance

Officials of Commonwealth Natural Gas Corporation of Richmond, Va., were impressed in 1956 with the many advantages of Polyken protection. With confidence based on the cathodic protection needs of their Polyken tape-coated 1956 Bellwood line (*inset photo*), they put this coating to work two years later on their Chester to Petersburg, Va., line (12 miles of 18″ pipe). In 1959, *more* Polyken coating . . . Waverly to Ivor, Va., (15.8 miles of 12″ pipe). And most recently, the line from Boswell's Tavern to Gum Spring (*main illus.*).

It stands to reason that repeated use is founded on first-hand satisfaction and trust. Many discriminating companies make Polyken protection their standard specification because of its dependable performance. Get full details on Polyken performance and economy from your representative, or write Polyken Sales Division, 309 West Jackson Boulevard, Chicago 6, Illinois.

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Plastic Society Schedules Eight Regional Meetings

Eight regional meetings have been scheduled by the Society of Plastics Engineers. Topics and dates for these meetings are given below.

April 4-5: Plastics Injection Moldwing Workshop, Holy Cross College, Worcester, Mass.

April 20: Plastics—A New Dimension in Buildings, Springfield Museum of Art, Springfield, Mass.

May 9: Plastics in the Automotive Industry, Detroit, Mich.

June 14: Plastics in Packaging, Montreal, Quebec, Canada.

September 12: Plastics for Tooling, Hotel Severin, Indianapolis, Ind.

October 5: Plastics Foams, Niagara Falls, N. Y.

November 2-3: Plastics in Packaging, Sheraton-Dallas Hotel, Dallas, Texas. Engineering Exhibition on November 1-3.

December 1: Plastics Screw Injection Molding, Cleveland Engineering Society Bldg., Cleveland, Ohio.

Additional information can be obtained from the society at 65 Prospect St., Stamford, Conn.

ASTM President to Speak March 9 at Houston Meeting

A. Allan Bates, president of American Society for Testing Materials and vice president of the Portland Cement Association will talk on "American and Soviet Construction Materials for the Future" at Houston Engineering and Technical Societies building on the evening of March 9. He will speak at a joint dinner meeting of Southwest District ASTM and Houston Branch, American Society for Civil Engineers. Additional information can be obtained from R. D. Wilde, Humble Oil & Refining Co., Houston.

Expanded Uses of Zinc, Galvanizing to Be Studied

A joint research and development program to expand the uses of hot dip galvanizing has been launched by the American Hot Dip Galvanizers Association and the American Zinc Institute. The program is to stimulate research and experiment by architects, engineers and technicians in many fields where hot dip galvanizing is not being used to its fullest potential and to encourage product improvements.

High Temperature Research Technical Services Offered

A new technical service which will deal with nickel alloys at elevated temperatures has been established in the Development and Research Division of International Nickel Company, Inc., 67 Wall St., New York 5, N.Y. This High Temperature Engineering Section, headed by NACE member F. L. LaQue, will develop and disseminate technical information in the field of high temperatures and will be prepared to give advice on selection of proper materials for high temperature applications.

•

Greater Boston Section will hold a corrosion short course June 20-21 at the Wentworth Institute, Boston, Mass.

•

Sale of books in the United States totaled $630 million in 1959.

Procedure Improved for Ordering Copies of Papers

Improvements have been made in the procedure for handling orders for copies of technical papers to be given at the 1961 NACE Buffalo Conference. The revised procedure is as follows:

1. Orders will be taken at Buffalo for copies of papers to be printed by NACE at a uniform price of 50 cents per copy, payment with order.

2. A list is published in this issue of CORROSION of papers to be printed by NACE. Orders will be accepted at 50 cents per copy for these papers from persons attending the conference. Orders from persons who did not attend will be accepted at $1 a copy.

3. Order forms will be at the NACE booth at the Corrosion Show.

Papers ordered from NACE will be printed and forwarded within six weeks after the Buffalo Conference.

Glass Reinforced Phenolics Used for Turbine Housing

Glass reinforced phenolics and polyesters have been used for a gas turbine compressor housing instead of the usual magnesium alloys, according to a paper presented at the recent conference of the Society of Plastics Engineers in Washington, D. C.

Estimates indicate that cost of the plastic compressor housing is about half that of conventional metals, resulting from drastically reduced machining that is not necessary on plastics. Close tolerances can be achieved with the plastics without additional machining operations required with metal alloys.

Performance of the turbine was improved because of reduced expansion of the plastic housing, according to the authors of the technical paper. Higher air pressures could be maintained to give greater turbine efficiency.

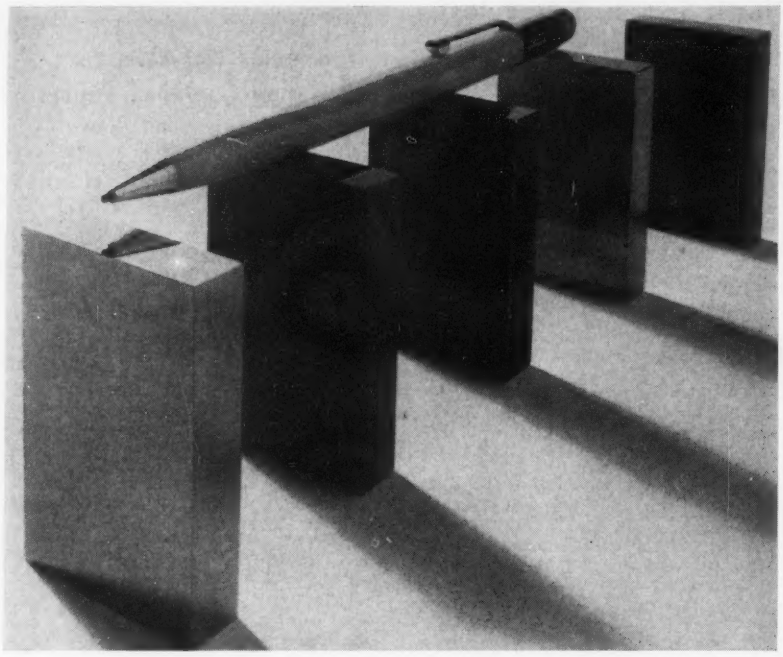
International Finishes Convention to Be May 8-11

Hot dip galvanizing and metallic and plastic coatings will be included in the papers to be presented during the First International Industrial Finishes Convention scheduled for May 8-11 at Earls Court, London, England. Other papers will be on paint finishing methods, chemical polishing, water soluble resin finishes, developments in aluminum finishes, chromium plating and high temperature paint curing techniques.

Additional information can be obtained from Scientific Surveys Ltd., 97 Old Brompton Road, London S.W.&.

Gas Distribution Meeting

The Distribution Committee of the Pennsylvania Gas Association will hold its 4th Annual One-Day Distribution Conference at the Tally Ho Inn and Hotel, Valley Forge, Pa., on April 6.



GAGE BLOCKS checked for stability at the National Bureau of Standards. At the left is one of the most promising blocks made by the Bureau of nitrided Type 410 stainless steel. The mirror-like finish of its gaging surface makes it particularly suitable for precision measurement. The other blocks (left to right) are a commercially manufactured experimental solid aluminum oxide, a nitrided 410 stainless steel with non-gaging faces unground after nitriding, a martempered stabilized 52100 block and a martempered stabilized 52100 block.

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Stainless Steel Used for Highly Stable Gage Blocks

In a long-range research program aimed at an accuracy of one part in 10 million in gage block calibrations, the National Bureau of Standards recently has made significant advances with the development of highly stable blocks and ultraprecise measurement techniques. Three types of gage blocks, produced by M. R. Meyerson of the Bureau's metallurgy laboratories, show dimensional stability considerably greater than the best commercial blocks. To obtain precise data on the small dimensional changes occurring in the blocks special measurement techniques were devised.

Gage blocks, carefully made of steel to exact dimensions, are used to monitor manufacturing processes in the mass production of interchangeable machined parts. As reference standards for such high-precision manufacturing operations as the making of machine tools, ball bearings and missile control mechanisms, gage blocks must be capable of providing measurements precise to within one part in one hundred thousand and with the advent of the space age, to one part in a million. Therefore, as the length of a block must be known even more accurately than the measurement referred to it, gage blocks certified to one or two parts in 10 million must be available soon on a regular basis.

To meet increasing demands for precision, the Bureau is focusing attention on characteristics of the gage blocks and on equipment and methods for measuring these blocks. Because of the industrial importance of this work, a group of private firms is helping to support the metallurgical research underlying the fabrication of precision gage blocks and the developmental metrology basic to achieving calibrations of the required accuracy.

Gage Block Metallurgy

Special effort is being made to develop gage blocks that will retain their calibrated lengths to high accuracy over a considerable period, with much less shrinkage or growth than is normally expected of precision gage blocks. At the same time, other requirements for gage blocks can not be neglected. These include an appropriate coefficient of thermal expansion, a high degree of surface finish, flatness of surface, parallelism of opposite gaging faces and resistance to wear, deformation and atmospheric and fingerprint corrosion.

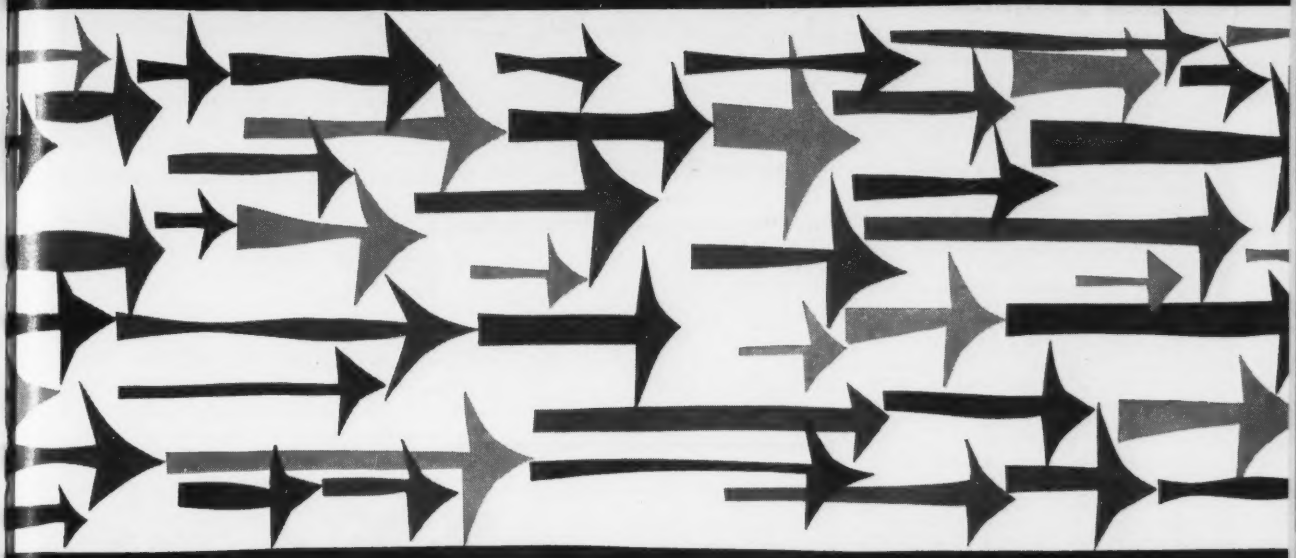
Dimensional instability in steel blocks is brought to result from structural changes in the hardened unstable structure formed during heat treatment and subsequent redistribution and relaxation of fabrication stresses. Therefore, a properly fabricated block of fully annealed steel of low alloy content, at or near its equilibrium condition, should be free from subsequent structural changes. However, such a block is too soft to use as a gage block because an adequate surface finish cannot be applied. Wear is high, and the surface is easily deformed. An alternate approach is to lower residual stresses in hardened steels by stress relieving in the vicinity of 1000 F, but this process also makes most hardened steels too soft.

To produce a hard wear resisting surface on the annealed material, the Bureau nitrided several steels, chromium plated some, coated others with either tungsten carbide or aluminum oxide and sprayed others with nickel-chromium-boron alloy. Attempting to improve the hardened steels, the Bureau tried to eliminate as many unstable constituents as possible and to reduce fabrication stresses. Some blocks were case hardened on the surface through the processes of carbonitriding, carburizing and cyanide hardening.

Sufficient data have been obtained on blocks of 410 stainless steel and 52100 modified steel to indicate that such methods can result in greatly improved stability. Annealed 410 stainless blocks with nitrided surfaces have been produced which exhibit a growth of only 0.0000002 inch per inch per year during the first year of observation. And 52100 steel gage blocks, given special stabilizing and stress relieving treatments, display a shrinkage of 0.0000004 inch per inch per year. At present, 16 materials are under investigation and have been given a total of forty-two different treatments.

Foundry Changes Name

Electric Steel Foundry Company, 2141 North West 25th Ave., Portland 10, Ore., has changed its name to Esco Corporation. The new name, previously used as a trade name for products, was developed because the former titled was not descriptive of the company's complete activities as a manufacturer, warehouse and foundry.



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ONE epoxy coating for internal coating of pipelines has been field tested on large diameter gas transmission lines. Just one. That is Copon.

The results of the industry field tests show that deliverability can be increased—"an additional one to six per cent increase directly attributable to internal coating."

We'll be glad to send you reprints of the feature articles in *Pipe Line Industry* and *Gas* which report these tests in detail.

The increase in pipeline thru-put revealed in these tests is a welcome *bonus* you get when you coat with Copon. Primary benefits of Copon internal pipe coatings include maximum corrosion protection—reduced maintenance costs . . . delivery of cleaner products.

Special applications are available for coating dehydrated gas lines, crude petroleum product lines, salt water or fresh water lines, and oil well tubing and casing.

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Use Copon to coat submerged or buried lines. Also on individual joints for new construction.

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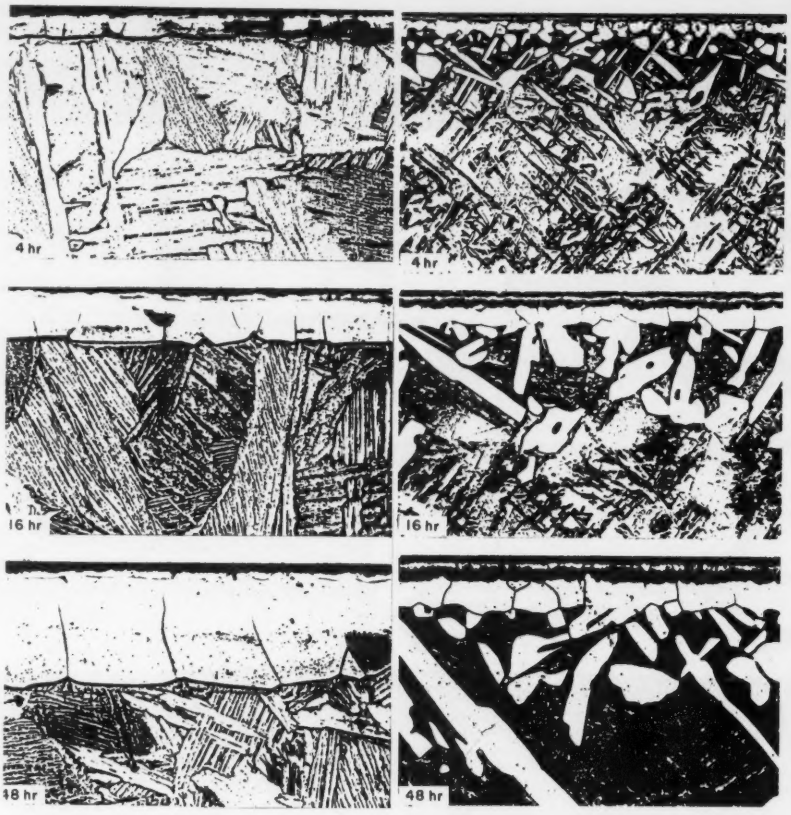
Carrier Based Planes Have Fuel Valves of Nitrided Titanium

Nitriding gives a desirable hardness to the surface of commercially pure titanium but has an adverse effect on the Ti-6Al-4V alloy, according to a National Bureau of Standards study for the Navy Bureau of Weapons. As a result of the study, fuel control valves for jet engines of carrier based aircraft have been experimentally produced from unalloyed titanium and nitrided. These nitrided titanium parts have displayed good performance characteristics in this application.

Proposed increases in temperature and pressure to improve aircraft engine performance will place increased demands on the durability of metals. Such materials must resist galling and wear between surfaces in sliding contact, must have good resistance to impact and to salt water corrosion, be light in weight, and exhibit good machinability.

This NBS study was undertaken because the nitriding process often increases the surface hardness of metals. Titanium inherently has excellent salt water corrosion resistance and a strong affinity for nitrogen, so it was a logical choice for a starting material. The alloy containing six percent aluminum and four percent vanadium had recently come into widespread use. Also, investigators reported vanadium to be the only alloying element other than boron that increased the diffusion rate of nitrogen through titanium. This alloy was therefore of particular interest.



NITRIDING gives a desirable hardness on pure titanium but adversely affects the Ti-6Al-4V alloy. Photomicrographs in the left row are titanium specimens; the alloy in the right row. Both were nitrided in purified nitrogen at 1800 F for the following times: top row, 4 hours, middle row, 16 hours and bottom row, 48 hours. Specimens were etched in one part HF (48 percent), 12 parts HNO_3 (concentrated) and 87 parts water. (144X)

Over 300 specimens used in the experiments were nitrided in purified nitrogen at 1800 F for 4, 16, 24, 48, 96 or 168 hours to obtain data on the relation between case thickness and duration of the treatment. A nickel-base alloy tube with water cooled ends was used as a nitriding chamber. Each specimen, individually drawn into the hot zone by magnetic attraction acting on an attached iron bob, was held at the nitriding temperature for its prescribed time, then magnetically drawn into the cool zone.

After cooling to room temperature, the nitrided specimens were analyzed metallographically. Analysis showed that the unalloyed metal forms a uniformly thick, hard case with a sharp line of demarcation between case and core. The nitride surface layer on the Ti-6Al-4V alloy is thinner than that which forms on the unalloyed titanium. Elongated nitride grains form in the alloy and penetrate as far as the center of the core at a 45-degree angle with the surface.

Impact strength of titanium, as determined by transverse impact tests on unnotched specimens, was not impaired as a result of the nitriding. However, after being subjected to the same treatment, the alloy exhibits a serious reduction in its impact resistance. The elongated nitrided grains in the alloy apparently act as stress raisers to reduce impact strength.

Subsequent examination of the alloy with an electron-probe micro-analyzer indicated that the vanadium content in the elongated grains was only one-half of that in the surrounding matrix. Also traverses across the boundaries of the elongated nitride grains indicated no vanadium composition gradient in the matrix in the vicinity of the boundary, but rather an abrupt change in vanadium from the level in the nitride grain to the level in the matrix. Thermodynamic data obtained from the experiments showed that the aluminum content plays a prominent role in the formation of the grains and confirmed the electron probe results in regard to vanadium.

The uniformly thick, nitrided case on the unalloyed titanium was a surface film 0.0005-inch thick, covering a principal layer of 0.004 inch, on specimens treated for 48 hours. Total case thickness increased with increase in nitriding time, following a parabolic law, and reached a thickness in excess of 0.008 inch in 168 hours. This behavior is contrary to that observed previously by other investigators, who found that titanium, nitrided in ammonia, attains a maximum case of approximately 0.004 inch and that further treatment reduces case thickness.

POSITIONS WANTED AND AVAILABLE

Active and Junior NACE members and companies seeking salaried employees may run two consecutive advertisements annually without charge under this heading, not over 35 words set in 8 point type. Advertisements to other specifications will be charged for at $12.50 a column inch.

Positions Wanted

Research & Development engineer, registered mechanical. Good chemistry background; 16 yr experience design, testing, application valves; familiar metals evaluation, coatings, plastics, elastomers, adhesives, lubricants petrochemical, chemical process services. CORROSION Box 61-4.

Sales Engineer—Experienced in analyzing corrosion problems, sales of protective coatings & linings, application or installation of materials. Desire sales or service position in corrosion control work. Resume on request. Willing to relocate. CORROSION, Box 61-2

Positions Available

CORROSION ENGINEER—E. E. degree. Ten years' experience in corrosion control engineering, design, installation, personnel training, standardization practices for transmission and distribution companies. Experience in sales engineering of corrosion control products. Will relocate. CORROSION, 61-3.

Metallurgist with corrosion engineering experience wanted for staff position, civil service, project management Army guided missile weapons systems. Write W. H. Ewart, Chief, Engineering Requirements, Coordination Office, Research & Development Operations, Army Rocket and Guided Missile Agency, U. S. Army Ordnance Missile Command, Redstone Arsenal, Alabama.

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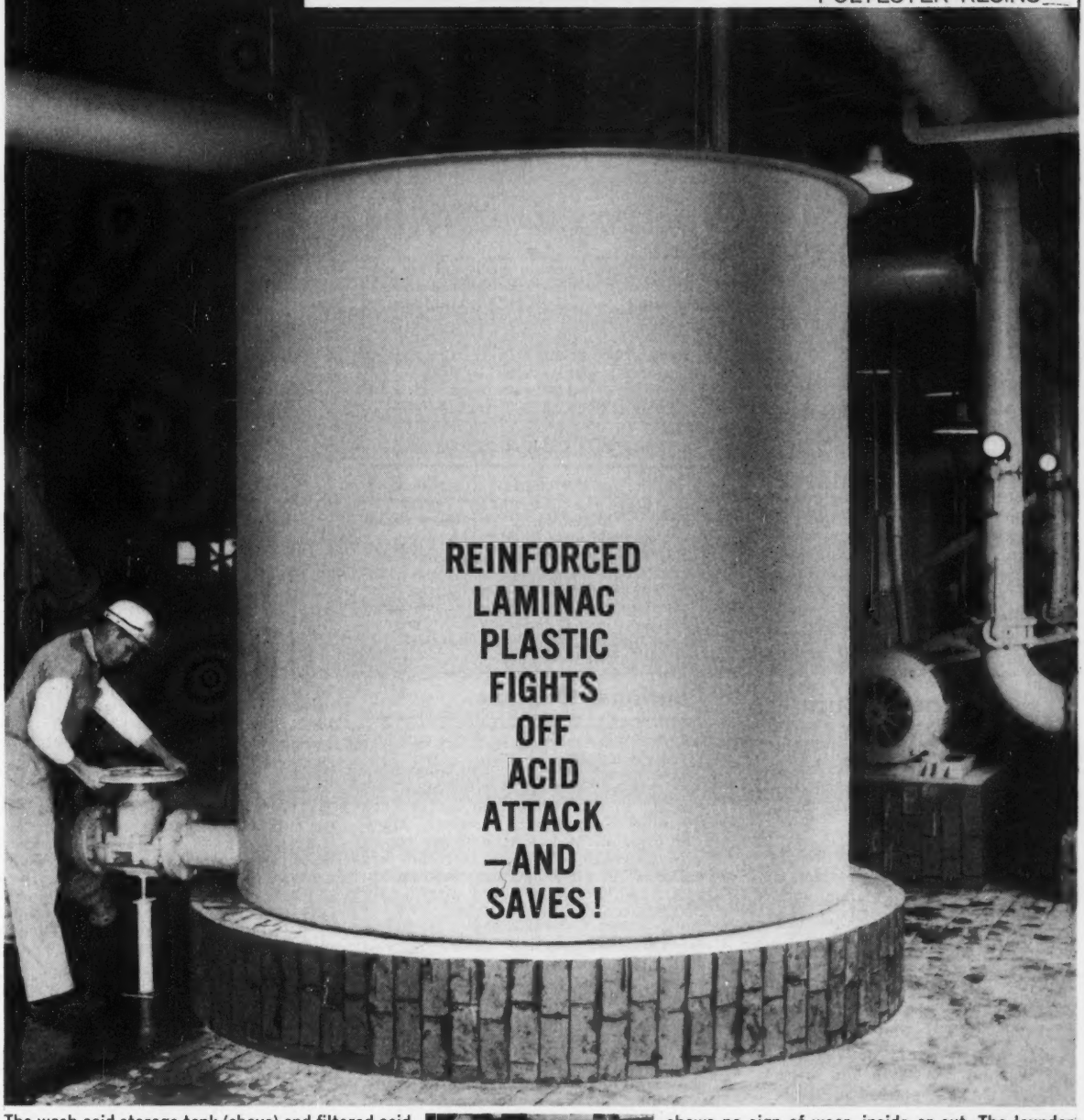
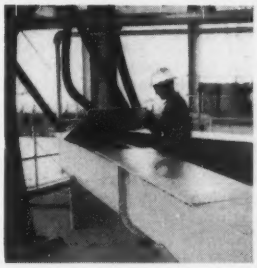


The wash acid storage tank (above) and filtered acid launder (at right) are two of many pieces of corrosion-resistant equipment recently installed in one of the country's large phosphoric acid plants. Manufactured of glass-reinforced Laminac polyester resin by the Corite-Reynolds Corp., Des Plaines, Ill., the equipment solves all of the plant's corrosion problems—and costs less to install in the bargain • Where other materials are damaged by abrasion and corrosion by phosphoric acid, sulphuric acid and gypsum, reinforced Laminac polyester resin



shows no sign of wear, inside or out. The launder handles a steady flow of wet process phosphoric acid of various strengths—without harm. The storage tank receives wash acid of 5-10% P_2O_5 phosphoric acid at 50°C.—and comes through unharmed. Reinforced Laminac requires no maintenance...helps to produce a contaminant-free, high purity product • Find out about reinforced Laminac, the material that has been solving industry's toughest corrosion problems. For details or technical assistance, get in touch with any Cyanamid office listed below.

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WALLINGFORD, CONNECTICUT. *OFFICES IN:* BOSTON • CHARLOTTE • CHICAGO • CINCINNATI • CLEVELAND • DALLAS • DETROIT • LOS ANGELES MINNEAPOLIS • NEW YORK • OAKLAND • PHILADELPHIA • ST. LOUIS • SEATTLE • *IN CANADA:* CYANAMID OF CANADA LIMITED, MONTREAL • TORONTO

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NEW PRODUCTS

Coatings, Application Equipment

Spray gun nozzles made of a variety of materials with a wide selection of spray angles are being manufactured by Associated Precision Industries, 6459 N. Sheridan Rd., Chicago 26, Ill. Nozzles are available in brass, Monel, steel, stainless steel, hard rubber and Teflon in spray angles from 15 to 180 degrees. Orifice diameters are from 0.010 to 0.546 inches.

●

An atomizing nozzle designed to give a uniformly atomized, solid-cone mist in capacities to 330 gph is manufactured by Schutte and Koerting Company, Cornwells Heights, Bucks County, Pa. Nozzles are available from stock in bronze and stainless steel in orifice sizes from 2 to 6 mm. Special corrosion resistant nozzles can be ordered.

Coatings, Conversion

A single dip chromate conversion coating process for cadmium to prevent tarnishing and corrosion has been developed by Hanson-Van Winkle-Munning Company, Church St., Matawan, N. J. Called Chem-Rite C-55, the process produces a clear chromate coating used chiefly to protect hardware and other cadmium plated products that require long shelf life without discoloration and loss of brightness.

Coatings, Organic

Clear urethane sealers keep concrete floors in industrial plants in good condition up to three times longer than other types of commercial sealers, according to tests conducted by Trancoa Chemical Corporation, Reading, Mass. The urethane sealers have shown resistance to water, chemicals, solvents and abrasion. Normal activity can be resumed within three hours after application, according to Trancoa.

●

High build-up at low rates of shear with rapid gelation rates is claimed for a new stir-in type dispersion resin designed for plastisol and high solids, low solvent organosol dip coatings. Designated as Bakelite vinyl resin QXKV-2, the resin has given good performance in rotation and slush molding applications and in machine applied coatings, according to the manufacturer, Union Carbide Plastics Co., 270 Park Ave., New York 17, N. Y.

●

A heavy duty epoxy coating containing lead silico chromate, iron oxide and leafing type pigments is described in a bulletin available from Wisconsin Protective Coating Corp., Green Bay, Wis. Designed for good bonding qualities and high chemical resistance, the coating can be used as a combination primer and coating and can be applied to thicknesses of 4 to 5 mils in one spray coat application, according to the manufacturer. Because no organic inhibitors are included, this primer can be used in immersion service. Physical properties, application procedures and recommended uses are given in the bulletin.

●

New series of organosol coatings called Sterilkote 360 is claimed to give good metal adhesion with only one application and without primer. The coating is a vinyl resin based and can be applied by manual, automatic or electrostatic spray equipment as well as by regular and reverse roll-coaters. Baking cycles are flexible and can be varied to suit different production ovens, according to the formulator, Bradley & Vrooman Company, 2629 South Dearborn St., Chicago 16, Ill. The coating is designed to have flexibility and high resistance to humidity, water, salt spray, peeling, chipping, flaking and marring.

●

A new polyvinyl chloride bonded type pipe coating for underground gas and oil transmission lines is being marketed by Wooster Finishes Corp., Plastic Coatings Division, Spruce Street Extension, Wooster, Ohio. Known as PTS-59, this modified plastisol pipe coating can be thermally bonded to all sized pipe. According to the manufacturer, a thin, 20-mil film thickness provides protection for severe corrosion conditions because no inorganic or metallic fillers are used. A bulletin diving details on the coating is available from Wooster Finishes.

Filters

A light weight, miniature filter assembly for fluid line systems handling caustic or corrosive liquids has been developed by Dumont Engineering Corp., 1401 Freeman Ave., Long Beach, Cal. In addition to its uses in aircraft and missles, the filter can be used in petroleum and chemical processing as a filter for instrument and gaging points. It has been in service with gases to 2250 psi and will withstand temperature extremes from —350 F to 500 F, according to Dumont. The unit is 1⅛ inches square and about 2 inches in length. It is made of stainless steel except for an enclosed, chemically inert plastic washer used to seal the two body halves together.

●

Replacement cartridge demineralizer with a 25 gph capacity and a direct reading purity meter calibrated in ppm impurities and ohms resistance has been developed by Barnstead Still and Sterilizer Co., 322 Lanesville Terrace, Boston 31, Mass. The unit can be operated at pressures to 100 psi. The cartridge holder is steel lined with PVC; the demineralizer head is faced with tin. The unit is only 6 by 8 by 26 inches.

Instruments

A potentiometer-voltmeter designed to give non-engineering personnel a simple, suitable meter for routine testing is available from Agra Engineering Co., 1537 East 10th St., Tulsa, Okla. Called the Dacca Pipe-to-Soil Voltmeter, it measures potential under any resistance conditions with an accuracy of 2.13 percent or better, according to Agra Engineering. Meter range is 0 to 1.5 volts with sensitivity of 10,000 phms per volt.

(Continued on Page 48)

NOW... X·TRU·COAT

the new polyethylene coating to prevent pipeline corrosion

FROM HILL HUBBELL

the name synonymous with quality pipe coatings and wrappings

If you are responsible for specifying pipeline protection, or keeping your pipelines as trouble-free as possible, then you'll find the above announcement important for two reasons.

First, because of the many desirable features inherent in high-density polyethylene X-Tru-Coat. *It has proven ability to resist a wide variety of soil conditions. It can withstand severe bending and flexing without damaging the protective continuity of the coating. It is easy to handle and install. Initial sizes: ¾" nom. to 5 9/16" O.D.*

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Any manufacturer's pipe can be coated. Strategically located plants of foremost technical design provide unmatched nationwide delivery. Buy pipe at your advantage and store in Hill Hubbell's yard until required on the job. Flexibility of specifications, scheduling and shipping can be tailored to your requirements. Only the finest materials are mill-applied under carefully controlled conditions. Factory to field assistance is always available.

These benefits are yours with *Hill Hubbell X-Tru-Coat* or one of the more than 30 other Hill Hubbell corrosion-control specifications.

Specify **Hill Hubbell X-Tru-Coat** *or other high-quality coatings mill-applied by Hill Hubbell, on your next job.*

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Hill Hubbell X-Tru-Coat is produced under the Dekoron® process.

NEW PRODUCTS

(Continued From Page 46)

Direct reading of conductivity for water treatment is possible with a pocket size meter manufactured by Comroe Laboratories, Inc., 5208 Lake Park Ave., Chicago 15, Ill. Designed specifically for the water treatment field, the instrument eliminates the need for time consuming laboratory instrument readings and permits immediate adjustment of chemical additives when needed, according to the manufacturer.

•

An illustrated catalog describing instruments for corrosion control engineering and geophysical subsoil surveys has been published by Associated Research, Inc., 3777 West Belmont Ave., Chicago 18, Ill. Catalog includes description of push-button measurement of soil resistivity, anode resistance, circuit resistance and polarization effect.

•

Checking alloys and new metal systems under dynamic conditions for resistance to stress and corrosion is one potential application of a new pulsed X-ray system developed by Zenith Radio Research Corp., 6001 West Dickens Ave., Chicago 39, Ill. Including a new long-life X-ray tube, the system uses a Rauland image intensifier tube which amplifies the X-ray image and converts it to visible light which appears as a bright image on the tube's output phosphor. The image is suitable for direct viewing, closed circuit television or for pick-up by motion picture cameras, according to Zenith.

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Plastics

Centrifugal blower housings made with a reinforced thermosetting resin with standard fan wheels also covered with the resin have been designed and developed by Ceilcote Company, 4832 Ridge Rd., Cleveland 9, Ohio. Called Duracor, the resin is formulated for extreme chemical resistance and high strength-weight ratios. The blower units can be installed as separate components in existing systems or integrally designed into exhaust systems.

•

Newly designed fluorocarbon spargers for injecting steam and other vapors below the liquid level in reaction vessels are available from Resistoflex Corporation, Roseland, N. J. Made of Fluoroflex-TF (Teflon), the spargers are claimed to have high resistance to mechanical fatigue, thermal shock and corrosion. They are internally reinforced with steel.

•

Teflon's lack of resilience as a sealing material has been overcome by use of an internal expander, according to Tanner Engineering Co., 1003 Santa Fe Ave., Los Angeles 21, Cal. Stainless Steel or synthetic rubber expanders are used, depending on the environment. The expanders maintain a continuous force against the sealing surface. The system has been patented as the Tec-Ring.

•

Molded screws made of acetal resin polymer are being injected molded by Gries Reproducer Corp., New Rochelle, N. Y. Made of du Pont's resin called Delrin, the screws are claimed to have high tensile strength, rigidity and resistance to deformation and high dimensional stability over a wide range of environmental conditions. The screws are claimed to be resistant to corrosive fluids such as gasoline, carbon tetrachloride, hydraulic fluids and oils.

•

A new division to provide design assistance and manufacturing facilities for pilot and full scale production of filament wound reinforced plastic parts has been established by Taylor Fibre Co., Norristown, Pa. The filament winding technique uses high strength glass filaments in tension to absorb loading stresses of a vessel. Applications include storage and processing equipment, pressure piping, pressure relief equipment and centrifugal spinning baskets.

•

A flush-toilet tank ball and guide designed to stop leakage and to prevent corrosion has been made of polyethylene resin by Valguard Co., Inc., Port Deposit, Md. The unit can be installed without tools and is claimed to be compatible with any flushing mechanism.

Tanks

To extend tank life and effectively combat corrosion, standardized storage water heaters are being fabricated from copper-silicon, Monel, Inconel, aluminum, nickel-clad and stainless-clad steel by Niagara Weldments, Inc., 55 Portage Rd., Niagara Falls, N. Y. Also standard steel tanks can be supplied with various linings and coatings such as phenolic, porcelain, cement or hot dip galvanizing. These tanks are marketed under the name NiaWel. A bulletin giving complete information on the tanks is available from the manufacturer.

Valves

A new bulletin on Tufline compact valves with sleeves, diaphragms and covers of Teflon is available from Continental Manufacturing Co., 230 Park Ave., New York 17, N. Y. The bulletin gives diagrams, suggested applications and describes corrosion resistance of the valves.

•

No threading, swaging, flaring, welding or special tools are required to install stainless steel tubing valves capable of handling liquids and gases at 12,000 psi, according to the manufacturer, Autoclave Engineers, Inc., 2949 West 22nd St., Erie, Pa. Called AE SpaceSaver valves, they are made of Type 316 stainless and are available in sizes for ⅛, ¼ and ⅜ OD tubing. Complete information is available from Autoclav Engineers.

•

Engineering specifications of corrosion resistant valves are given in a bulletin available from Alloy Steel Products Co., Linden, N. J. Chemical composition ranges and minimum mechanical properties are included in this Corrosion Resistant Valve Bulletin No. 7.

MEN in the NEWS

NACE Member Jean S. Wood has joined the sales staff of Geigy Industrial Chemicals, Saw Mill River Rd., Ardsley, N. Y., to represent the company in Texas, Louisiana, Oklahoma, Mississippi and Arkansas.

•

Raymond C. Baxter has been appointed vice president of engineering for Allied Chemical's National Aniline Division, 40 Rector St., New York 6, N. Y.

•

Paul J. Chaney has been appointed vice president of Sumitomo Shoji New York, Inc., 149 Broadway, New York 6, N. Y., where he will manage the newly formed Tubular Products Division.

•

Jerome B. Cohen of Northwestern University, Evanston, Ill., Department of Materials Science, has been named winner of the AIME's Metallurgical Society's Robert Lansing Hardy Award.

•

Herbert J. Cooper has been named president and chief executive officer of Cooper Alloy Corp., Hillside, N. J.

•

William W. Hays has been appointed marketing manager of Atlas Powder Company's chemicals sales department, Wilmington 99, Del.

•

Two new vice presidents have been named for Graver Tank and Mfg. Co., 4809 Tod Ave., East Chicago, Ind., **Henry H. Hemenway** becomes vice president for research and engineering; **Lionel G. Lancaster** becomes vice president for construction. **Willard M. Broxham** has been named vice president and Pacific Coast sales manager.

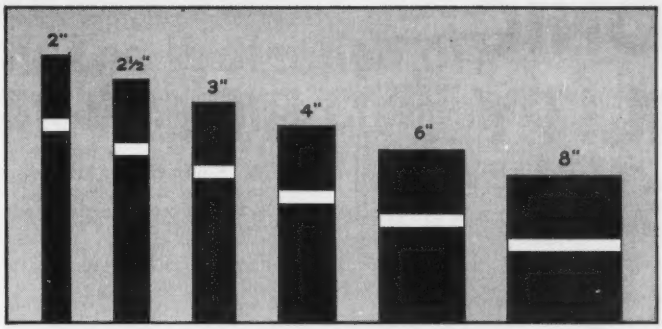
•

William A. Hopkins has been appointed electroplating product specialist for Metal & Thermit Corp., at the company's Detroit, Mich., offices.

•

James M. Hughes has been appointed sales manager of regular products for Dresser Manufacturing Division of

(Continued on Page 50)



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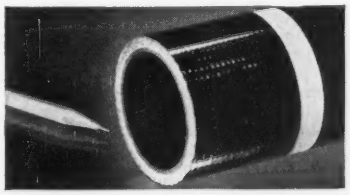
Now! A complete size range of Fibercast Epoxy Pipe—including new 6″ and 8″

- *handles a temperature range from −65° to 300° F.*
- *withstands an operating pressure range up to 1200 psi.*
- *pipe sizes from 2″ to 8″*

Only Fibercast, with its unique reinforced epoxy resin construction, can withstand sustained high pressures, high temperatures and extreme corrosive conditions more efficiently than any other pipe. Fibercast's ability to competently handle 320 of 338 corrosive solutions is on record. And now Fibercast, in answer to more of the needs of industry, brings its proven value to larger size flow lines.

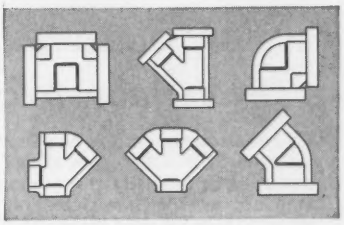


Fibercast Tube and Pipe, ranging in size from 2″ to 8″, is not subject to cold flow or permanent set. It is exceptionally easy to install, readily following ditch contours, saving many costly man-hours where other non-metallic pipes or coated metal pipes simply do not work effectively.

The operating collapse strength of Fibercast is another major factor in its wide-spread use. It has a proven capability of maintaining a collapse load of *twice* the rated collapse!* Moreover, Fibercast is much lighter than steel (less than ¼ its weight) and is correspondingly easier to handle, during both installation and maintenance.

**An additional safety factor is that Fibercast, with its seamless woven glass fiber construction, cannot burst.*

Fibercast Fittings, of course, are also available for the new sizes. They represent the world's most complete stock of standard sizes and types. And, as always, you can have couplings, or even complete piping systems, designed and made to order for your individual requirements.



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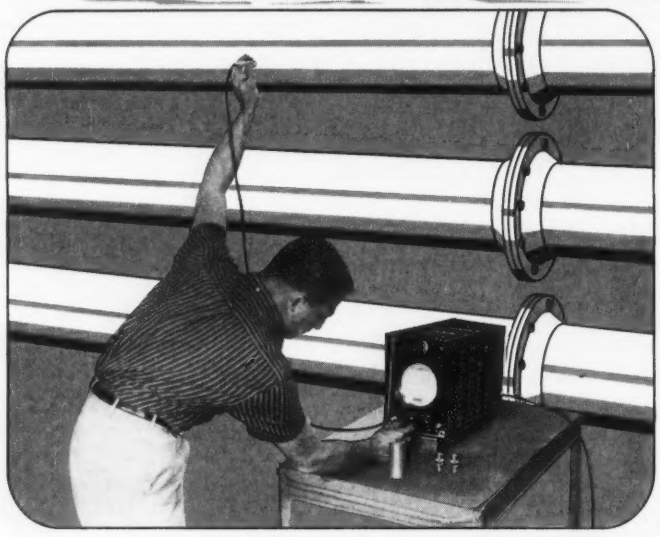

The Variable Angle Beam Transducer

This new transducer has been specially engineered for angle beam testing with the SONORAY® flaw detector. It incorporates a variable collimator designed to intensify the ultrasonic beam when needed. In addition to standard internal flaw detection, the variable angle beam transducer is also suitable for weld inspection and thickness gaging. The transducer is interchangeable in order to make the frequency fit the job. There are two versions of the variable angle beam transducer presently available: One for continuous water flow and the other with stationary water inside the shoe. The outstanding advantages are:

- Continuously adjustable for all angles, from straight to surface wave.
- Interchangeable transducer and beam collimators.
- Suitable for high temperature work and rapid surface scanning.
- Selection of shoes, flat or curved, to fit the surface of the work piece.

The variable angle beam transducer is further proof of the technical ingenuity and know-how of Branson's Ultrasonic Test Division. The next time you have a testing problem call BRANSON and see how fast BRANSON will find the best solution in the shortest possible time.

SINCE 1946 — THE RESPECTED NAME IN ULTRASONICS

BRANSON INSTRUMENTS, INC.

Ultrasonic Test Division
52 Brown House Road, Stamford, Conn.

MEN in the NEWS

(Continued From Page 48)

Dresser Industries, Inc., Bradford, Pa. He will direct sales of pipe joining and pipe repair products.

•

D. W. Kaufman has been named product manager of stainless steels for Crucible Steel Company of America, Pittsburgh 22, Pa.

•

William L. McMahon is sales representative in the Milwaukee area for Pittsburgh Corning Corporation, 1 Gateway Center, Pittsburgh 22, Pa. His office will be at 1024 East Ogden Ave., Milwaukee, Wis.

•

Robert G. Meihls has been named district sales manager of the middle Atlantic states for Hill Hubbell Co., 3091 Mayfield Rd., Cleveland 18, Ohio.

•

Ronald P. Remorenko has been promoted to assistant chief research engineer for Fafnir Bearing Co., 37 Booth St., New Britain, Conn.

•

Dowell Sellers is sales development manager of plastic materials for construction, B. F. Goodrich Chemical Co., 3135 Euclid Ave., Cleveland 15, Ohio.

•

NACE Member **R. W. Maier,** immediate past chairman of the Pittsburgh NACE Section, has been transferred from the Pittsburgh general office of Gulf Oil Corporation to the Materials Engineering Division of Gulf Research & Development Co., Harmarville, Pa.

•

Lawrence O'Hanlon has been appointed chief design and application engineer for the filter division of the Meaker Company, Nutley, N.J., subsidiary of the Sel-Rex Corporation.

•

David W. Lillie has been named manager of the Materials Application and Evaluation Section of the General Electric Research Laboratory, Schenectady, N.Y.

•

NACE Member **Edward T. Wanderer** has been appointed development manager of machinery and equipment, a new position in Aluminum Company of America's development division, 1501 Alcoa Bldg., Pittsburgh 19, Pa. **Ralph L. Horst, Jr.,** another NACE member, has been named manager of Alcoa's chemical and petroleum section.

•

John W. Paterno has been appointed a technical representative in the metropolitan New York sales region for Union Carbide Plastics Co., division of Union Carbide Corporation. He will be located in the company's office at 1051 Bloomfield Ave., Clifton, N.J.

•

Ralph W. Rawson will be general manager of the Chemical and Metallurgical Division of Fansteel Metallurgical Corporation at Muskogee, Okla. This division is a consolidation of the former chemical and metals fabrication divisions.

•

NACE Member **Merrill A. Scheil** has been elected national secretary of the American Society for Metals. He is director of metallurgical research for the A. O. Smith Corp., Box 584, Milwaukee, Wis.

Truscon Makes Massive Breakthrough In The Protection of Steel Against Corrosion . . . With

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From the laboratories of Truscon . . . a galvanic material that provides *new control* in the field-coating of structural steel, tanks, dam gates and other on-shore and off-shore installations.

CHEM-ZINC is a *ready-mixed* zinc-filled coating that cures to an inorganic film. It is a single-application, complete, anti-corrosive coating. It can be over-coated, if desired, in as little time as 20 minutes at 77° F.

CHEM-ZINC PROVIDES THESE DISTINCT ADVANTAGES . . .

- Maximum control because it's ready-mixed. No chance for improper mixing at job site.
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- Resistant to rain, splash, turbulence and immersion in fresh or salt water—minutes after coating.
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Paper No.	TITLE	COPIES
4	Nitrogen Tetroxide Corrosion Studies, by C. W. Alley, A. W. Hayford and H. F. Scott, Jr.	
8	Corrosion Characteristics of Iron-Aluminum and Iron-Chromium-Aluminum Alloys in the Petroleum Industry, by R. B. Setterlund and G. R. Prescott.	
9	Oxidation of Iron-Chromium Alloys, by D. Lai, R. J. Borg, M. J. Brabers, J. D. Mackenzie and C. E. Birchenall.	
11	The Influence of Variables on the Corrosion of Copper-base Alloys in Refinery Systems, by Mahmoud T. Dajani and David B. Boies	
12	The Effect of Redox on Refinery Corrosion, by C. B. Hutchison and W. B. Hughes.	
18	Painter Safety, by L. S. Hartman.	
23	Versamid-Epoxy Coatings—Corrosion Applications, by Harold Wittcoff, Don E. Floyd, David W. Glaser and Donald L. Andersen.	
24	Protective Coatings for High Temperature Service, by Gatewood Norman.	
29	A Method for Prevention of Hydrogen Embrittlement of Tantalum in Aqueous Media, by C. R. Bishop and Milton Stern.	
30	Titanium-Use in Oil Production Equipment, by Ricardo Molina and F. W. Jessen.	
32	The Casing Inspection Tool, An Instrument for the In Situ Detection of External Casing Corrosion in Oil Wells, by T. R. Schmidt.	
34	A Basis for Design of Aluminum Alloys for High Temperature Water Service, by R. L. Dillon and H. C. Bowen.	
41	Inhibition Studies in Reactor Decontaminants, by Ronald D. Weed.	
	TOTAL	

Paper No.	TITLE	COPIES
45	Corrosion Research and Control in Eldorado's Beaverlodge Mill, by G. F. Colborne, A. R. Allen and A. Thunaes.	
48	The Use of Pipe-To-Soil Potential in Analyzing Underground Corrosion Problems, by Bernard Husock.	
54	The Electrochemical Approach to Cavitation Damage and Its Prevention, by H. S. Preiser and B. H. Tytell.	
56	Magnesium Anodes for the Cathodic Protection of Naval Vessels, by L. J. Waldron and M. H. Peterson.	
59	Corrosion of Superalloys at High Temperatures in the Presence of Contaminating Salts, by A. Moskowitz and L. Redmerski.	
61	Iron Sulphate for Condenser Tube Control, by T. W. Bostwick.	
64	The Unique Role of Plastics in Corrosion Control, by Raymond B. Seymour.	
65	Plastic Pipe Systems For Corrosion Resistance, by Allyn E. Webb and R. W. Johnson.	
67	A New Design for Reinforced Plastic Tanks, by W. R. Wardrop and F. H. Humphrey.	
70	Theory and Application of Deep Ground Beds, by J. F. Tatum.	
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NACE NEWS

Two More NACE Short Courses Are Scheduled

Two more NACE corrosion short courses have been scheduled for 1961. They are the June 7-8 short course to be sponsored by the Teche Section at the University of Southwestern Louisiana at Lafayette, La., and the September 27-29 short course sponsored jointly by the Central Oklahoma Section and the University of Oklahoma. This second short course will be held on the University of Oklahoma campus at Norman. It will be the eighth annual corrosion control short course held at the University of Oklahoma.

Other short courses on corrosion are listed in the calendar of national and regional meetings on Page 58.

1962 CHAIRMAN for the 18th Annual NACE Conference will be Robert H. Goodnight (center), who is manager of heavy duty finishes division of Cook Paint & Varnish Co., North Kansas City, Mo. At left is NACE Executive Secretary T. J. Hull, and at right NACE Exhibition Manager R. W. Huff, Jr., discussing plans with Mr. Goodnight for the Kansas City meeting and 1962 Corrosion Show. Committee chairmen being selected for the 1962 Conference are scheduled for publication in the May issue. An NACE member since 1951, Mr. Goodnight is chairman of Technical Committee T-6B-17 (Chemical Cured Coal Tar Coatings) and has been a speaker at the Tulsa Section Short Course.

Canadian Region

Toronto Section officers for 1961 recently elected are as follows: Chairman G. K. Dudgeon of British American Oil Co., Vice Chairman J. G. Fillo of Bell Telephone, Secretary D. Dowan of Corrosion Service Ltd., Treasurer G. L. Stone of Glidden Paint Co., Membership Committee Chairman R. E. Gamey of Bell Telephone, Program Committee Chairman W. H. A. Henderson of Electric Reduction Co., and Trustee H. A. Webster of Corrosion Service Ltd.

T. J. Maitland of American Telephone and Telegraph, New York City, spoke on engineering cathodic protection systems for communications cables at the January meeting attended by 31 guests and members.

•

Montreal Section heard H. Sadoughi of Quebec Natural Gas Corporation speak on cathodic protection of underground pipelines at the March 4 meeting.

The section held a joint meeting on January 24 with the Steam and Steam Power Section of the Canadian Pulp and Paper Association. About 140 attended. Guest speaker was R. T. Hanlon of Alchem Limited, who spoke of the causes and prevention of corrosion in condensate systems.

NACE members who have not paid their 1961 association dues will be removed from mailing lists to receive CORROSION magazine and other association publications, effective March 31, 1961.

This is in accordance with provisions in the NACE Articles of Organization and By-Laws.

Photographs and News Stories on Buffalo Conference

Photographic coverage and news stories on the 17th Annual NACE Conference and 1961 Corrosion Show in Buffalo will be published in a special section of the April issue of CORROSION Magazine.

Western Region

San Francisco Bay Section Plans 4 Future Programs

Program plans through September, 1961, have been made by the San Francisco Bay Area Section. Dates, speakers and topics are given below. No meetings are scheduled for June, July and August.

March 20: Modern Chemical-Synthetic Coatings for Marine, Marine Atmosphere and Tank Ship Ballast Tank Applications by John R. Saroyan of Naval Paint Research Laboratories.

April 14: Experiences With Underground Cathodic Protection, by Kent Lundergan of Electro-Rust Proofing.

May: Barbecue and tour of winery.

September 12: Applications of Cathodic Protection, by Paul Offerman of Standard Oil Company of California.

1961 Officers Elected

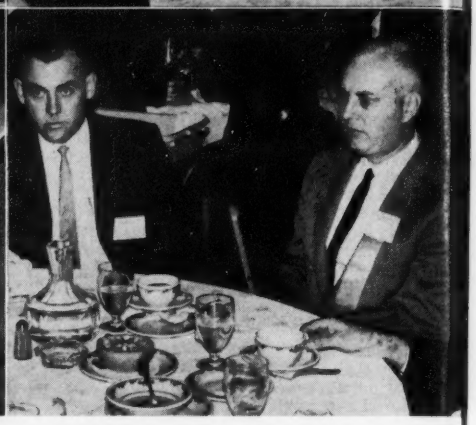
Section officers recently elected for 1961 were installed at the January 10 meeting. They are Chairman Ernest F. Ehmke of Tidewater Oil Co., Associated, Cal., Vice Chairman George E. Moller of Union Oil Co., Rodeo, Cal., and Secretary-Treasurer Glenn P. Snarr of Bunker Hill Co., Oakland, Cal.

•

The 1961 Western Region Conference will be held at the Benson Hotel, Portland, Ore., October 4-6.

•

NACE's 18th Annual Conference and 1962 Corrosion Show will be held at the Municipal Auditorium, Kansas City, Mo., March 19-23, 1962.



RECORD ATTENDANCE of 306 is partially shown in upper left photograph of the opening session of the Houston Short Course. In upper right photograph is one group at the luncheon. Left to right are J. R. Brock, vice president of Service Painting Co., Beaumont, Texas, M. J. Moreau of California Co., Harvey, La., W. D. Sanford of California Co., Barataria, La., and George W. Gartner, Jr., of the F. W. Gartner Co., Houston. One of the informal discussion groups that took place between formal sessions is shown in lower left: A. A. Dunbar of Humble Pipe Line Co., Longview, J. M. Brooke of Phillips Petroleum Co., Sweeny, Texas, Jack Corbin of Nalco Chemical Co., Houston, and R. Comeaux of Humble Oil & Refining Co., Baytown, Texas. In lower center photograph are Edward T. O'Rourke and Kirby L. Boston of Pittsburgh Plate Glass Co., Houston, and H. D. Collingsworth of Armco Steel Co., Houston. In the center background is F. Parker Helms, one of the short course lecturers. In lower right photograph is General Chairman of the short course, J. A. Caldwell of Humble Oil & Refining, Houston in the center with James R. Boswell on the left and Bill Koehler on the right, both from Humble.

Houston Sets New Enrollment Record

A record enrollment of over 300 attended the February 2-3 corrosion control short course sponsored by the Houston Section at the Rice Hotel. Registrants came from nine states and Mexico, with 80 percent of the enrollment attending the short course for the first time.

Registrants also represented all levels of industry from top executives to field technicians. Fifty percent of the attendants were from oil production, 20 percent from pipelines, 20 percent from refineries and chemical plants and the remaining 10 percent included men from utilities and engineering consulting firms.

•

Central Oklahoma Section has scheduled Charles Hudgins to speak on corrosive properties of clear completion fluids at the April 10 meeting.

Ray M. Hurd, vice president and research director of Texas Research Associates in Austin, Texas, will speak on the effect of molecular structure on chemisorption and corrosion inhibition at the March 6 meeting.

•

Teche Section saw two films on cathodic protection for its February 8 meeting. The films were shown by Jack Davis of Cathodic Protection Service, Houston.

•

Alamo Section heard J. W. Gibson speak on anodic protection at its January 19 meeting.

•

North Texas Section has scheduled a talk by Joe Rench of Napko Corp., Houston, on protective coatings for the March meeting.

•

East Texas Section officers elected for 1961 are Chairman John Luttig, Vice Chairman Gene E. Smith, Secretary T.

(Continued on Page 57)

South Central Region

1961 SHREVEPORT SECTION officers are (seated left to right) Vice Chairman D. A. Tefankjian of Texas Eastern Transmission Corp., Chairman Grady F. Howell of Tube-Kote Company, Secretary John W. Graves of United Gas Pipe Line Co., and (standing left to right) Treasurer W. E. Moore of Tretolite Co., and Trustee M. J. Olive of Corrosion Control Associates.

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	*Proc. Short Course on Process Industry Corrosion	20.00	25.00			Sulfide Stress Corrosion—A Symposium	3.50	5.00	
	*High Purity Water Corrosion of Metals	7.00	9.00			Ground Anode Tests First Interim Report	3.00	5.00	
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	*Control of Pipe Line Corrosion by O. C. Mudd	1.25	1.25			Testing 32 Alloys in Flow Stream of 7 Condensate Wells	8.00	10.00	
	Cathodic Protection—A Symposium	6.00	8.00			Correlating Committee Report on Cathodic Protection	.50	.50	
	1945 Bibliographic Survey	4.00	5.00			Mitigation of Underground Corrosion—J. M. Pearson	2.50	2.50	
	1946-47 Bibliographic Survey	7.00	9.00			10-Year Index to CORROSION	2.50	2.50	
	1948-49 Bibliographic Survey	10.00	12.50			Stress-Corrosion Cracking of Austenitic Stainless Steels (NACE and ASTM Report)	4.80	6.00	
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	1952-53 Bibliographic Survey	10.00	12.50			Sulfide Corrosion—Three Papers	1.00	1.00	
	1954-55 Bibliographic Survey	15.00	20.00			High Silicon Cast Iron Anodes—Second Report	1.50	2.00	
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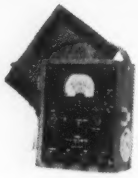

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North Central Region

CLEVELAND SECTION OFFICERS for 1961 are as follows: (seated in front, left to right) Chairman Peter P. Skule and Trustee John Scott; (standing left to right) Vice Chairman W. H. Hooker, Secretary-Treasurer Robert Schantz, Program Chairman E. Vereekee, J. F. Bosich, member of National Nominating Committee and A. V. Higgins, member of Advisory Committee of the section.

Eastern Wisconsin Section has planned its programs through May as follows:

March 6: Practical applications of cathodic protection, by H. F. Haase of Chain Belt Co., Milwaukee, and L. C. Wasson of A. O. Smith Corp., Milwaukee.

April 10: Latest Developments in Metal Spraying Plus Plasma Arc Process, by C. J. O'Boyle of Metco, Inc., Chicago, Ill.

May 8: Corrosion Resistance of Copper Alloys and Aluminum Alloys, by Wilson Lynes of Revere Copper and Brass, Rome, N. Y.

J. D. Malone of Boshopric Products, Cincinnati, Ohio, spoke on epoxy coatings for corrosion control at the February 13 meeting.

Walter R. Pasco of the Polymer Corp., Reading, Pa., discussed fusion bond coatings, a new technique for plastic cladding metal, at the January 9 meeting.

New officers for the section are Chairman R. D. Eberhardt of Allis-Chalmers, Vice Chairman T. E. Johnson of Stainless Foundries and Engineering, Secretary-Treasurer L. C. Wasson of A. O. Smith Corp., Recording Secretary T. Quick of the Ladish Company and Trustee D. D. Walczyk of A. O. Smith Corp.

•

Twin City Section heard Bernard Husock of Harco Corp., Cleveland, Ohio, discuss cathodic protection with impressed current at the February 14 meeting.

For its January meeting, the section held a field trip to the Northern States Power Company's Black Dog power plant.

•

Chicago Section had T. J. Maitland of American Telephone and Telegraph Co., New York City, speak on engineering cathodic protection systems for communication cables at the January 17 meeting, attended by 48 members and guests.

•

Southwestern Ohio Section had 59 guests and members for its January 31 meeting at Dayton. A tour of the Duriron Company plant and a panel discussion of cathodic protection were included.

LaQue to Be Corporate Luncheon Speaker

Frank L. LaQue, vice president of International Nickel Co., Inc., New York, N. Y., will be the speaker at the NACE Corporate Member Luncheon to be held Tuesday, March 14 during the 17th Annual Conference in Buffalo, N. Y. The luncheon is scheduled to be in the Golden Ballroom of the Statler-Hilton Hotel, conference headquarters.

A past president of NACE, Mr. LaQue will talk on the subject "Management's Stake in Corrosion Control."

NACE Members Omitted From Congress Author List

Three NACE members were omitted from the list of authors on Page 57 of the February issue, who will participate in the First International Congress on Metallic Corrosion, April 10-15, in London, England. They are D. A. Shock, J. D. Sudbury and O L. Riggs of Continental Oil Co., Oklahoma City, Okla. Their paper to be presented at the congress is entitled "Use of Anodic Passivation for Corrosion Mitigation of Iron and Alloy Steels."

1961 APPALACHIAN UNDERGROUND Short Course Publicity Committee discussed promotion of the June 6-8 short course during its meeting in Pittsburgh, December 1. Standing left to right are William Andrews of Dresser Industries, John Vrable of New York State Natural Gas Co., and William Cook, Jr., of Pipeline Service Corp. Seated left to right are Dale Miller of Corrosion Magazine, Lance Heverly of Trans-Canada Pipelines, Ltd., Publicity Committee Chairman John H. Alm of Dearborn Chemical Co., and Nick Panetta of Michigan Consolidated Gas Co.

Greco to Give Opening Address At Appalachian Short Course

NACE President-elect Edward C. Greco of United Gas Corp., Shreveport, La., will present the opening address at the Sixth Annual Appalachian Underground Corrosion Short Course to be held June 6-8 at West Virginia University, Morgantown.

Greco

The program as planned to-date lists about 65 papers for presentation during the course, covering basic, intermediate and advanced sessions on corrosion control as related to underground pipe, cable and water systems.

Ten new subjects have been added to the short course. Other features of the course are field demonstrations of corrosion control equipment, a three-hour open discussion on corrosion problems and an exhibit of materials and equipment in the corrosion control field.

A record attendance of 600 registrants attended the 1960 short course. Sponsored by West Virginia University and endorsed by NACE and American Water Works Association, the short course is considered one of the largest of its type. Sessions are designed to cover corrosion control topics for all job levels.

Additional information about the short course can be obtained from John H. Alm, 2 Gateway Center, Room 605, Pittsburgh 22, Pa.

Brian Cox Receives Young Author Award

Brian Cox of the United Kingdom Atomic Energy Authority's Chemistry Division in England has been named to receive the NACE Young Author Award for 1960.

The award is in recognition of his paper titled "Oxidation and Corrosion of Zirconium and Its Alloys" published in the April, 1960, issue of CORROSION.

The NACE Young Author Award is given annually for the paper considered the best published in CORROSION by an author not over age 35.

South Central Region

(Continued From Page 54)

S. Hickman, Treasurer L. W. Riall and Trustee Jack Rowe.

•

Houston Section had 42 students attend its Student Night Meeting January 10. Guest students were from Rice University, Lamar Technical College, University of Texas, University of Houston and Texas A & M College. Guest speaker was Ray M. Hurd, vice president of Texas Research Associates in Austin. He spoke on corrosion opportunities in engineering research.

S. John Oechsle, Jr., executive vice president of Metalweld, Inc., spoke on marine corrosion at the February 14 meeting.

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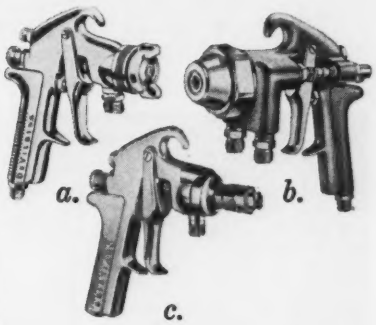

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SECTION CALENDAR

March

13 Kansas City Section.
13 Greater St. Louis Section. Process Industry Corrosion by A. S. Krisher.
13 Central Oklahoma Section.
13 North Texas Section. Torch Restaurant, Dallas, 6:30 pm.
14 San Francisco Bay Area Section.
14 Permian Basin Section.
14 Twin City Section
14 Montreal Section. Corrosion Problems Facing a Consulting Engineer.
16 Vancouver Section.
16 Alamo Section.
21 Chicago Section. Corrosion Contractors Panel Discussion.
21 Kanawha Valley Section, Marietta, Ohio.
27 Tulsa Section.
28 Panhandle Section.
28 Southwestern Ohio Section. Cincinnati, Ohio. Inhibitors and Chemical Treatments for Corrosion Protection, by William D. Gordon.

April

5 Schenectady-Albany-Troy Section: Ladies' Night. Corrosion in the Home, by E. A. Tice, International Nickel Co., Inc.
10 Eastern Wisconsin Section: Latest developments in Metal Spraying Plus Plasma Arc Process, by C. J. O'Boyle of Chicago.
10 North Texas Section.
10 Central Oklahoma Section. Corrosive Properties of Clear Completion Fluids, by Charles Hudgins.
10 Kansas City Section.
10 Greater St. Louis Section.
11 Houston Section.
11 Permian Basin Section.
11 Twin City Section.
12 Tidewater Section.
12 Greater Boston Section. Corrosion in Boilers and Condensate Lines, by Douglas E. Noll.
14 San Francisco Bay Area Section. Experiences with Underground Cathodic Protection, by Kent Lundergan of Electro-Rust Proofing.
18 Cleveland Section.
18 Chicago Section. Corrosion Problems in Nuclear Reactors, by Sherman Greenberg, Argonne National Laboratories.
18 Baltimore-Washington Section. Characteristics of Hot Dip Galvanized Coatings, by H. R. Breslau.
20 Vancouver Section.
20 Alamo Section.
24 Tulsa Section.
25 Panhandle Section.
25 Southwestern Ohio Section. Steels That Fight Corrosion, by John J. Halbig, Armco Steel Corp. To be held at Connersville, Ind.

NATIONAL and REGIONAL MEETINGS and SHORT COURSES

1961

March 12—NACE Board of Director's Meeting, Hotel Statler, Buffalo, N. Y.
March 13-17—17th Annual Conference and 1961 Corrosion Show, Buffalo, N. Y., Hotel Statler.
March 17—NACE Board of Director's Meeting, Hotel Statler, Buffalo, N. Y.
Oct. 4-6—Western Region Conference, Benson Hotel, Portland, Oregon.
Oct. 9-11—North Central Region Conference, St. Louis, Chase Park Plaza Hotel.
Oct. 24-27—South Central Region Conference and Exhibition, Shamrock-Hilton Hotel, Houston.
Oct. 30-Nov. 2—Northeast Region Conference, New York City, Hotel Statler.
Nov. 27-Dec. 1—Southeast Region Conference and Florida General Conference Short Course, Key Biscayne Hotel, Miami, Fla.

1962

March 19-23—18th Annual Conference and 1962 Corrosion Show. Kansas City, Municipal Auditorium.
October 1-4—Northeast Region Conference, Hotel Sheraton Ten Eyck, Albany, N. Y.
October 9-11—North Central Region Conference.
October 11-12—Southeast Region Conference, Birmingham, Ala.
October 16-19—South Central Region Conference and Exhibition, Granada Hotel, San Antonio.

1963

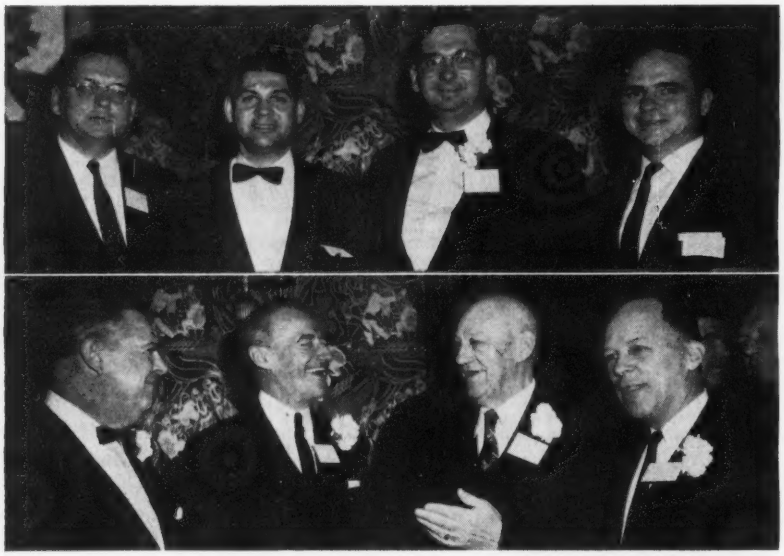
March 18-22—19th Annual Conference and 1963 Corrosion Show. Convention Hall, Atlantic City, N. J.
October 14-17—South Central Region Conference, Oklahoma City, Okla.

SHORT COURSES

1961

June 5-9—Corrosion Short Course, co-sponsored by NACE Greater St. Louis Section and Washington University, to be held at Washington University, St. Louis.
June 6-8—6th Annual Appalachian Underground Corrosion Short Course, University of West Virginia, Morgantown.
June 7-8—Teche Section Short Course, University of Southwestern Louisiana, Lafayette, La.
June 20-21—Greater Boston Section Corrosion Short Course, Wentworth Institute, Boston, Mass.
Sept. 27-29—8th Annual Central Oklahoma and University of Oklahoma Corrosion Control Short Course, Norman.

Northeast Region



OLD AND NEW OFFICERS were honored at the Metropolitan New York Section's Christmas Party. At top are shown the 1961 officers left to right: Chairman S. N. Palica, Vice Chairman R. E. Gackenbach, Trustee B. C. Lattin and Secretary-Treasurer G. W. Kurr. In bottom photograph are shown two founders of the section and two past chairmen: (left to right) W. B. Shaw (past chairman), L. Donovan (founder), E. P. Noppel (founder) and F. E. Kulman (past chairman).

Philadelphia Uses Phone Chain to Remind Members

Almost 80 members and guests attended the February 7 meeting of the Philadelphia Section despite unfavorable weather predictions and private and public transportation problems. The large attendance was attributed to a telephone chain set up by the section to remind members of the meeting.

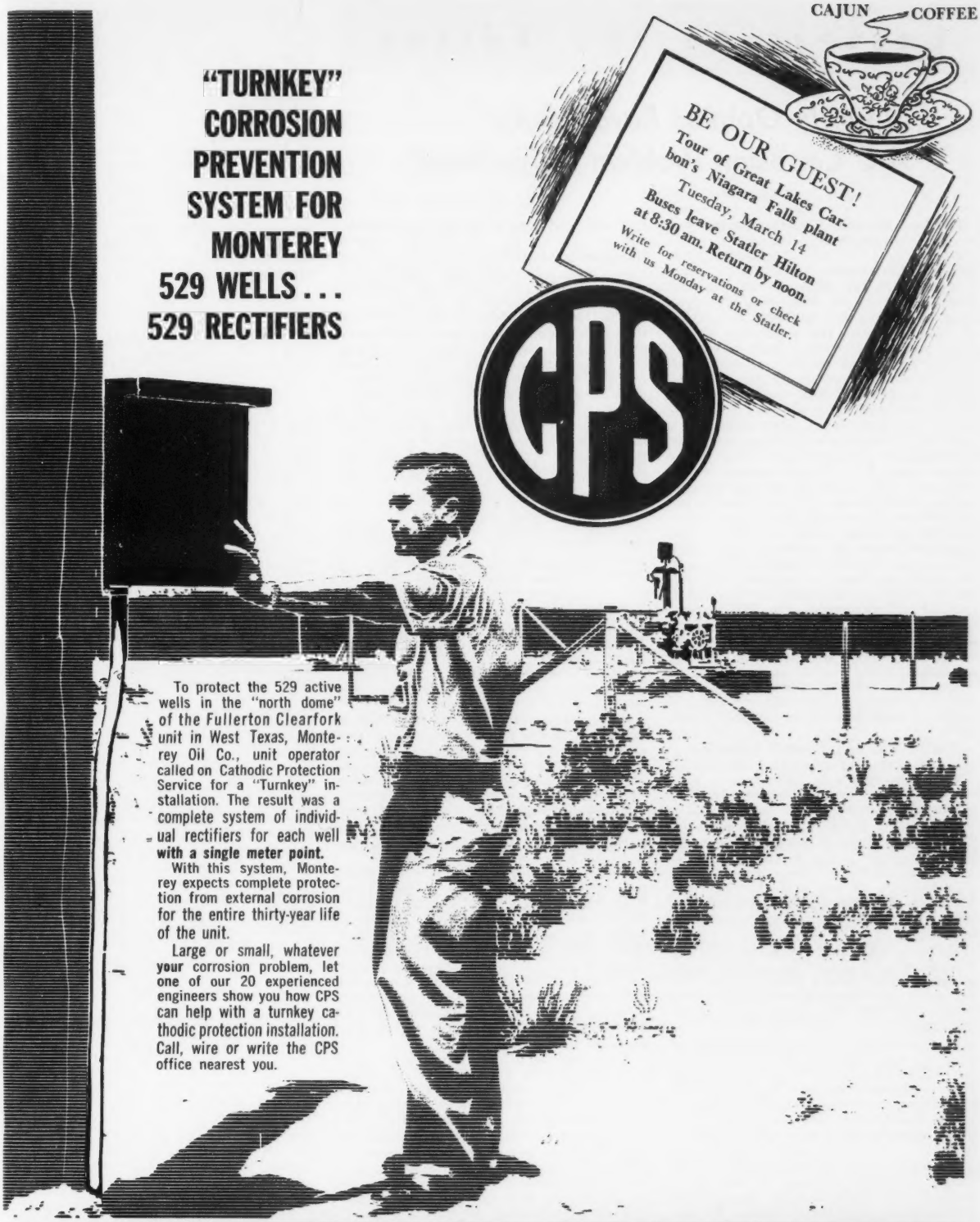
A panel discussion on coatings was held for the program, moderated by Edward Brink of American Viscose Corporation. Panel members were Kenneth Lefevre of Metalweld Corporation and Joseph Walters of Electro-Chemical Engineering & Mfg. Company.

•

Wilmington Section heard R. C. Canapary of Nalco Chemical Company speak on film-forming and anti-fouling inhibitors at the January 25 meeting.

•

Sale of books in the United States totaled $630 million in 1959.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Letters to the Editor

Majority Opinion Favors Belief A-C Corrosion Problem Insignificant

Portland General Electric Company
Portland 5, Oregon
August 23, 1960

Editor of CORROSION:

Your editorial (Beware of Ground Return Circuits in Electrification, August 1960) is going to bring you a lot of mail, because the corrosion conditions you deplore are caused by direct current or self-rectification of radio frequency currents, whereas the electric utility system "ground returns" mentioned are 50-60 cycle a-c which is technically and historically non-corroding.

In the USA, the use of the earth for a return on a-c circuits is very widespread, both for primary feeders, especially in REA construction, and in secondary distribution. No corrosion is attributed to these ground returns.

Even in those cases in which the "neutral" return is a metallic wire, this wire is grounded at many points and the earth becomes a parallel path for the currents. At substations where these parallel paths converge, the A-C ground currents are often very large, yet they do not corrode the ground system metal at the substation, whether it be of steel or copper.

Yours very truly,
Delmar L. Brown
Superintendent, Testing Dept.

Pacific Gas and Electric Company
Department of Engineering Research
Emeryville 8, California
October 18, 1960

Editor of CORROSION:

I am quite disturbed by the editorial "Beware of Ground Return Circuits in Electrification" in the August 1960 issue of "Corrosion."

It appears to me that this editorial does not properly differentiate between the effects of alternating and direct current electricity.

From a corrosion standpoint, the transmission of alternating current using ground return, cannot be compared with corrosion problems which have been caused by direct current used on street railways.

In my opinion, alternating current of common transmission frequencies does not cause corrosion. I am sure many other engineers working in the field of corrosion are of the same opinion, while a few believe a-c corrosion may sometimes occur under very special conditions.

At times there is considerable alternating current flowing in the earth, ground beds, ground rods, and various underground structures caused by unbalanced load conditions. We have never encountered a case of corrosion that could be attributed to this alternating current.

Many of the electrical utility companies are often being blamed for serious corrosion of customers' piping, hot water heaters, swimming pool equipment and other metallic structures because they have heard of the term "electrolysis" and readily assume their problem is caused by alternating current from some nearby transformer. Of the many such cases we have investigated over a number of years, none could be attributed to alternating current.

Until sufficient research has been done in the field of a-c corrosion to properly evaluate and specify what the special conditions are when a-c corrosion may occur, I feel that "Corrosion" has done a disservice to the entire electric utility industry by this editorial. I believe that "Corrosion" should publish a disavowal of such a drastic statement or as a minimum, point out the dissimilarity between the problems of a-c and d-c corrosion.

Yours very truly,
Roy O. Dean,
Senior Corrosion Engineer

The Electricity Authority of New South Wales
North Sydney, NSW
31 October 1960

Editor of CORROSION:

Beware of Ground Return Circuits in Electrification

Under the above heading "An Editorial" in Corrosion August, 1960, Volume 16, No. 8 page 7 refers particularly to dismay in learning that in Australia a scheme is in use whereby electric power is brought to rural areas using earth for return. To imply as is done in this editorial that such a practice will raise problems comparable with those resulting from the operation of direct current traction systems is a very serious allegation when no technical arguments are brought forward in substantiation.

Whilst such technical arguments were not to be expected in an editorial article, nevertheless The Electricity Authority of New South Wales has done much to encourage within this State the development and use of Single Wire Earth Return systems where particular economic considerations have warranted and would therefore greatly appreciate disclosure in your publication of the sources of information on which the conclusions were based.

Economic considerations enter very greatly into the problem and it would probably not be difficult to establish that in the "remote regions" where the system has been used the return from the investment will have justified installation within much less than the time mentioned in the editorial article and in any case the implied desirable conversion to an equivalent three-phase system would not then be difficult of achievement.

Whilst the remarks concerning high voltages involved cannot be taken seriously the suggestion of calamitous consequences arising from the sudden development of thriving industrial communities in the areas in this country where the system has been installed is not only unlikely but its solution would not daunt the engineering staff that would be concerned.

It is believed that there are a greater number of installations of Single Wire Earth Return systems in the State of Victoria and with respect to the editorial article in question the Sydney Electrolysis Committee working under the aegis of this Authority has contacted the Melbourne Electrolysis Committee within the State Electricity Commission of Victoria who are wholly in accord with this protest now being presented.

In conclusion it is repeated that it would be appreciated if some substantiation could be given or literature quoted that would explain some of the argument of the editorial and afford some guide as to why so much dismay has been felt.

S. E. Parry
(Chairman)

United States Department of Agriculture
Rural Electrification Administration
Washington 25, D. C.
October 12, 1960

Editor of CORROSION:

We have seen the article entitled "Beware of Ground Return Circuits in Electrification" in the August issue of CORROSION, and are concerned about misunderstandings that may result from it. The editorial is very appropriate in regard to direct current circuits, but unfortunately it does not mention the very important difference between direct currents and alternating currents in causing corrosion.

Effects of direct currents in the earth in causing corrosion are well known; in fact, the amount of metal removed due to a direct current can be estimated quite reliably from the measured current, and the valence and atomic weight of the metal. On the other hand, the corrosion effects of alternating currents in electric systems are so slight that they usually are not considered important. The same would be expected in radio-frequency systems.

There is a need for further study of conditions that may result in alternating current corrosion, as is pointed out by Mr. F. E. Kulman in his paper. However, we believe that the serious limitations upon ground return alternating current circuits arise because of limited capability of the circuits and increased difficulty in achieving safety, not in the likelihood of corrosion problems.

Orville W. Zastrow
Chairman, Committee T-4A
Effects of Electrical Grounding on Corrosion

Harry Farnsworth Brown
Consulting Engineer
New Haven, Connecticut
October 12, 1960

Editor of CORROSION:

Your editorial "Beware of Ground Return Circuits in Electrification" in the August issue of CORROSION will cause needless concern to many engineers dealing with corrosion problems who are not fully conversant with electric power distribution problems.

Alternating current should never be confused with *direct* or *continuous* current in so called "electrolysis" problems.

In this editorial, the problems of the economic distribution of relatively small amounts of isolated blocks of *alternating* current electricity supply to rural areas, by adequately grounding one side of a single-phase circuit at the supply transformer and at the several consumption points, and omitting the line con-

ductor between the grounded points, are being confused with and compared with the problems which still exist in many areas, both urban and rural due to stray *direct* current caused by the potential drop in the *rail* return circuit of street railways and other electrified railways using *direct* current for propulsion. The problems are not at all similar.

Alternating current has been used on electrified railways with *rail* return in this country for more than 50 years in large areas having many valuable investments in underground metallic structures. The important railways operating all the way from New Haven, Conn., to Washington, D. C., and to Harrisburg, Pa., have been and still are operated in this manner.

Regardless of how well bonded the rail return circuit may be on either alternating current or direct current railways, there will always be a large percentage of the return current leaving the rails due to their electrical resistance, and returning through the ground, whenever the car or train using this current is at a distance from the supply point or points. Some of this ground current may enter and leave any underground metallic structures in the immediate vicinity of the railway.

A certain amount of corrosion will always occur in any unprotected buried metallic structure, due to a number of local causes known to the corrosion engineer, even in areas remote from any electric power systems. The corrosion of such structures may become greatly augmented where stray *direct* current leaves such structures and re-enters the ground, unless protective or mitigative measures are taken.

In the cases where stray current from these railways electrified with *alternating* current has entered or left the underground metallic structures in these areas from or to the surrounding earth, it has never been conclusively proved that the corrosion of these underground structures has been augmented by the stray *alternating* current. The writer was for many years electrical engineer for one of these railways, and has worked with and conferred with the engineers of the various communication, power, water and gas companies having extensive underground cables and pipes, with their corrosion problems, in parts of this area, and can make this considered and unqualified statement:

During the period 1930-1940, and since the war, the Rural Electrification Administration applied to numerous rural areas in this country the very same single-wire, single-phase alternating current distribution scheme your editorial condemns for application in India.

Further, nearly every high tension electric power line in this country is connected at each end, and at taps or branches, to "wye" connected transformers, with their neutrals securely grounded. There are always possibilities of slight alternating currents due to any small phase unbalance, in the ground between these connections. Nearly all of these lines are protected by a "ground wire" carried above them. A small amount of *alternating* current is always induced in this wire from the power conductors, which is drained off to the ground at regular intervals, usually at each steel tower.

In nearly every home and commercial building in this country serviced with electricity, the electrical circuits of the *alternating* current power supply are securely grounded or connected to the water pipes for safety and protection, because it is well known that any stray *alternating* current can cause no appreciable underground deterioration of such pipes. The possibility always exists of some stray or balancing alternating current flowing from these pipes into the surrounding earth. If alternating current did cause appreciable corrosion to underground metallic structures, there is a greater hazard due to this grounding practice in our large cities, than could be attributed to any rural electrification scheme with ground returns.

1961 Corrosion Show Color Slide Presentation

A color slide-talk presentation covering the 1961 Corrosion Show and the 17th Annual NACE Conference in Buffalo will be available from NACE Central Office after April 15 for showings at section meetings and before other groups.

In the article referred to in the editorial relative to the cathodic protection of the Lacq Field Well Casings, in France, it should be pointed out that the stray current involved was from the railways electrified in this case with 1500 volts *direct* current.

The National Electrical Code, approved as an American Standard by the American Standards Association in 1946, has this to say about the grounding of alternating current systems in buildings:

> GROUNDING ELECTRODES
> 2581. WATER PIPE. A continuous metallic underground water piping system shall always be used as the grounding electrode where such piping system is available.

Obviously, such a rule would have been permitted only if it was the considered opinion of qualified engineers that no corrosion hazards are involved from alternating currents in underground metallic structures.

May I suggest that this editorial be modified and clarified.

Harry F. Brown
Member, NACE

Editor of CORROSION:

I wish to comment on the editorial on page 7 of your August edition captioned "Beware of Ground Return in Electrification." There can be no doubt that the author of this article is fully aware of the enormous difference—orders of magnitude—between the corrosion effects of alternating current as compared to that of direct current. He must, therefore, have overlooked the fact that the earth current in the system discussed by Atkinson & Garg **inherently** is **alternating** current also that, to insure against communication interference, the earth current will not exceed about 10 amperes in any area.

Not for your editor, who does not need the explanation, but for those of your readers whom it may help, it is worthwhile to point out the theoretical reasons for this difference as well as some of the data of practical experience. The big reason for the difference in the effect of a-c and d-c is the electro-chemical effect of the reversal. The hundredth of a second for the current to reverse in direction **does not give time** for corrosion products to diffuse away from the surface before the reversal of the current brings about the reverse of the chemical effect—the change from an oxidizing to a deoxidizing state. The result is a substantial neutralization of the action in the previous half-cycle. In addition the current flow in **one direction** for a given number of amperes of alternating current is only ½ as much as for the same number of amperes d-c. (Indeed, taking into account that the **average** value of a-c is somewhat less than the **effective**—the measured value—this factor is more than 2.) Others may prefer to express the difference between a-c and d-c in another manner but the distinction is clear to most engineers. Quantitative evaluation of the degree of difference

(Continued on Page 62)

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Letters to the Editor

(Continued From Page 61)

can best be made by reference to typical and extensive experience.

One particular application of large underground power transmission has given reason for careful systematic scientific and practical study of the characteristics of a-c with respect to corrosion. When large alternating currents are carried in single conductor lead-covered cables, very considerable alternating voltage is indeed between the sheaths and the surrounding earth (usually conduit). While lead sheaths have been very vulnerable indeed to electrolysis from d-c current, these cables have been remarkably free from damage due to this alternating voltage. (Actually **no** damage has been reported.) To insure against damage, it is common to limit the a-c potential from sheath to surroundings to about 15 to 25 volts. Such a voltage, if d-c, would commonly produce extremely rapid corrosion. Of course, the small a-c currents in the electrification projects discussed by Atkinson & Garg, will produce voltages from any underground structure to the surrounding earth of only a small fraction even of this value known from extensive experience to be fully safe. How extensive this practical experience is with a-c potential from underground metal in contact with the earth may be visualized from the following figures. Cables which operate with considerable a-c voltage to earth transmit a total of many millions of kilowatts of power. Thousands of miles and scores of millions of dollars worth of cables are involved.

Of course, all this does not mean that corrosion can not occur as a result of a-c; indeed it is known that corrosion can be caused by a-c. But does it mean that, only with fear and trembling can we accept underground flow of a-c of whatever magnitude? Does it mean, for instance, that even communication or signaling circuits cannot, if desired, use ground return? Obviously that is **reductio ad absurdum.**

But fear of significant corrosion due to current normally not exceeding 10 amperes is for practical purposes, quite as groundless. For example, commonly, in the case of our numerous rural and urban **multi-grounded power lines,** there are earth currents as great as this. There is little doubt that many of the numerous pipe lines of this country pass through the areas where there is such underground flow of alternating currents. It would be interesting to know whether any special means have been taken in these regions to provide against corrosion by alternating current. It is probable that no harm has come to the pipe lines passing through these regions even if no special means of protection are used; however, if protection is deemed desirable, the requirement could be readily and inexpensively met.

The whole point to be emphasized here is that the use of ground return as shown in the Garg-Atkinson paper does not introduce any conditions relating to corrosion that have not long existed harmlessly in this country.

R. W. Atkinson
Westfield, N. J.

October 20, 1960

Editor of CORROSION:

Comments On Editorial Page 7, August 1960 Issue

I have read the subject editorial with a great deal of interest and agree that the use of ground return circuits should be avoided. However, I feel that *alternating current* ground returns *will not* cause any particular problem from the standpoint of corrosion per se. I can see that some problems might occur where the return current will seek metallic structures and overload insulated joints, etc. hence causing difficulties with the operation of cathodic protection systems.

Inherent in such a system is the possibility of operating problems for the electrical power supplier and consumer due to unbalanced voltages in single phase systems and of safety hazards appearing where the metallic path is broken. Therefore, it is highly improbable that alternating current ground return systems will ever be adopted to any appreciable extent. Such systems are not sanctioned in the United States by the National Electric Code.

I feel that a definite operating and safety problem is involved but very little, if any, corrosion problem. Certainly this matter merits further consideration and study and going a little deeper into the problem that is done in the editorial. Without exception, I believe the editorial uses examples where *direct current* has caused a corrosion problem by ground return current rather than alternating current.

Your editorial might prompt some unthinking person to remove a-c grounds where they are needed for safety's sake.

Glyn Beesley

October 7, 1960

Editor of CORROSION:

On reviewing the letters from the readers of CORROSION, all of whom are associated with the electrical industry, the following thoughts are suggested:

The a-c electrified railroads use the running rail as the return conductor. The running rail is laid on wood ties set in well drained broken stone or gravel ballast. Thus only a minor portion of the current is returned via the earth. The designers apparently were aware of ground return circuits.

The REA overhead system carries a metallic return conductor which is grounded at numerous points. Again, only a portion of the current is returned via the earth.

Favorable experience with a-c voltages on bare lead sheath cables is not sufficient assurance that corrosion will not occur at coating breaks in a steel or aluminum pipeline.

Letters from people in the water industry are conspicuously absent but may start coming in when the present letters are published. These people hold views which would impute not only corrosion but bad odor and taste to alternating currents in water pipes.

If as much effort were expended in laboratory investigation of a-c corrosion as in defending opposing views we could forget about a-c corrosion where it does not exist and concentrate our efforts on mitigating it where the conditions favor its occurrence.

The American Gas Association is planning to have research on a-c corrosion started early in 1961.

F. E. Kulman

Editor's Reply:

Questions on A-C Corrosion Unanswered

We acknowledge an error in not distinguishing between d-c and a-c current. The term "stray current corrosion" has generally been concerned with d-c current and the dangerous effects of these currents are well known today. They were not generally recognized before the advent of cross-country pipelines. With the reduction in number of electric railroads and streetcars, this problem has disappeared in many areas.

However, the a-c current problem cannot be ignored. There are instances where the only explanation available attributes the corrosion to a-c current. J. D. Piper reported[1] that tower footings having ground connections corroded faster than those without. Aluminum conductors have suffered corrosion while energized with alternating current and submerged in water.[2] There is concern about effect of induced currents from overhead electric services on coated pipelines.

There is a need for more work in this area. The paper by F. E. Kulman presented to the 1960 American Gas Association Operating Section Distribution Conference is reprinted in this issue beginning on Page 34 with permission of American Gas Association. This article gives a historical review and summarizes the state of the existing knowledge. There are many unanswered questions, but this does not mean that we can ignore the problem. We firmly believe that there are dangers both from safety and corrosion standpoints when earth is used for return of current, whether it be d-c or a-c.

On a well-coated pipeline, induced voltages can arc across insulated flanges. To prevent this, pairs of zinc anodes were installed at the flanges to permit current to cross without arcing.[3]

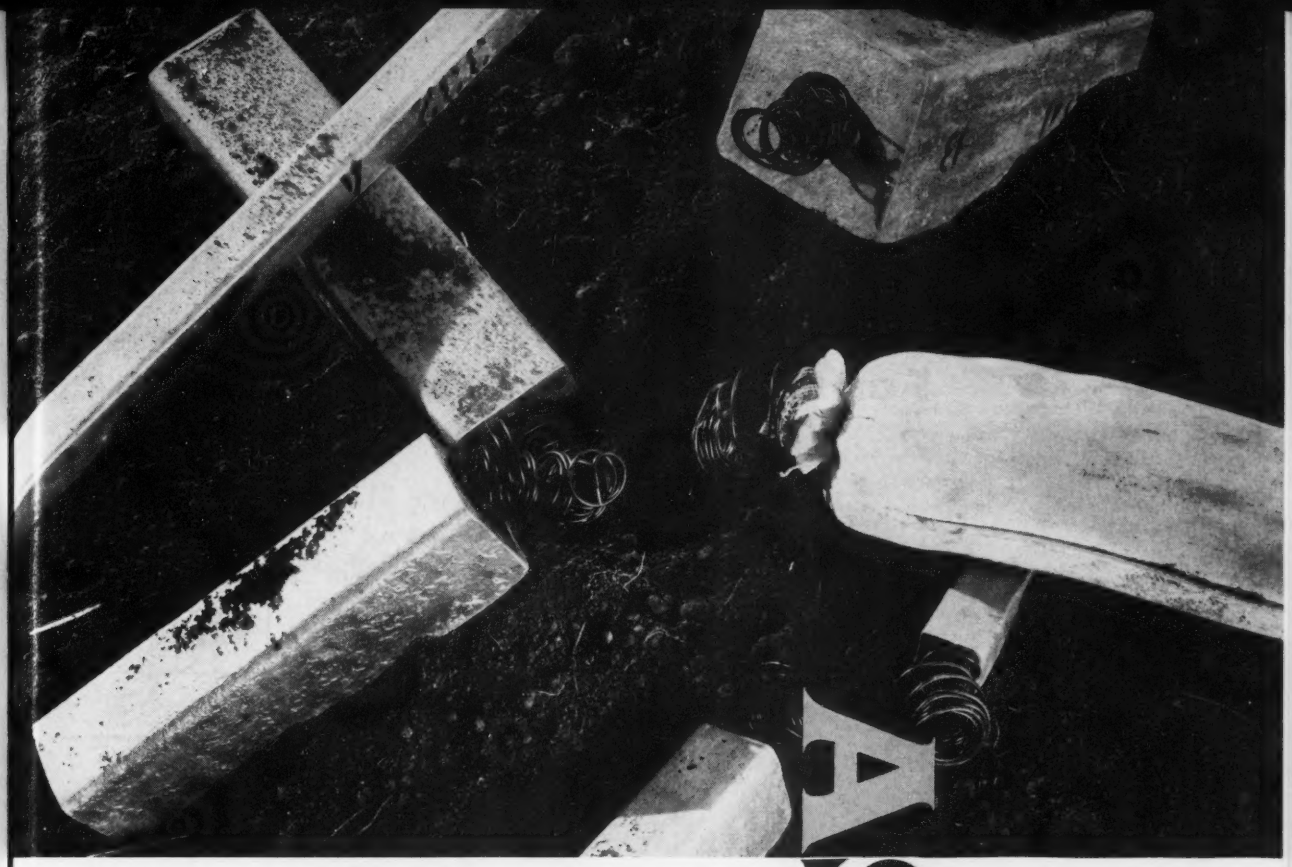
References

(1) *Corrosion*, **12**, No. 3, 119t-125t (1956).

(2) F. E. Kulman, NACE Project Group T-4B-1C on AC Corrosion. Aluminum conductors submerged in manhole water while energized at 120 volts with alternating current lost about two inches of the end of one conductor in about five months. Water contained chlorides, sulfates, carbonates and bicarbonates. In laboratory tests under similar conditions, aluminum cable corroded. The hypothesis explaining the reaction is that during the half-cycle when the aluminum is at negative polarity, an alkali (sodium hydroxide) is formed next to the aluminum. The alkali dissolves the normally protective film and some of the base metal. During the next half cycle, the current flows from the aluminum into the electrolyte, removing some of the aluminum and partly reforming the film. In time the layer of corrosion products formed tends to maintain an alkaline condition at the aluminum surface in spite of alterations in polarity.

This reaction apparently does not apply to other metals . . . lead, for example, which has operated for many years in some installations with 60-cycle voltages over 12 with respect to earth without apparent damage.

(3) E. H. Thalman, Galvanic Anodes Control Induced Voltages on Pipelines. *Corrosion*, **10**, No. 11, 367 (1954) November.



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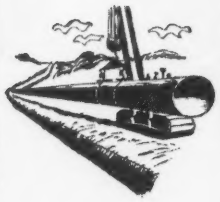

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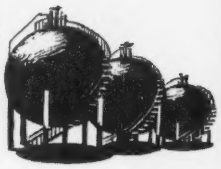

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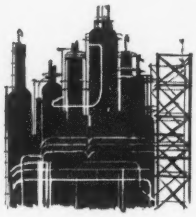

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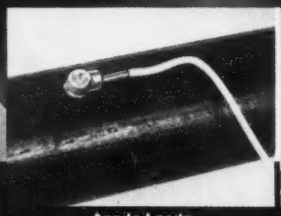

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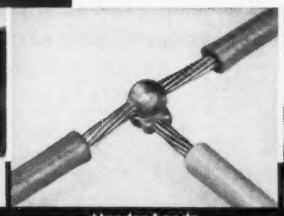

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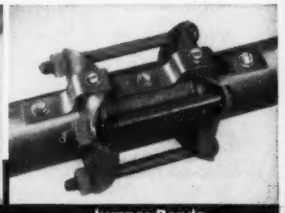

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CORROSION ABSTRACTS

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CORROSION ABSTRACTS

Vol. 17 March, 1961 No. 3

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3. CHARACTERISTIC CORROSION PHENOMENA

3.2 Forms

3.2.3, 3.7.4, 3.4.7, 6.3.6, 4.6.5

The Oxide Films Formed on Copper Single Crystal Surfaces in Pure Water. Pt. I. Nature of the Films Formed at Room Temperature. Jerome Kruger. National Bureau of Standards. J. Electrochem. Soc., **106,** No. 10, 847-853 (1959) Oct.

A study was made of the nature of the films that formed on carefully prepared surfaces of single crystals of copper immersed in water containing varying amounts of oxygen, with the surrounding atmosphere both controlled and uncontrolled. It was found that the amount of oxidation depended on the crystallographic orientation of the metal surface. Cuprous oxide was the oxide observed if pH $\leqq$ 5.7. Intense white light markedly retarded film formation in water. When cuprous oxide was formed, it had a perferred orientation and exhibited epitaxial relationships to the metal similar to those found in high-temperature oxidation. The films formed were not continuous but were composed of small nuclei of cuprous oxide. Both cuprous oxide and cupric oxide were formed at pH 7 when the water was in equilibrium with an atmosphere of pure oxygen. Lowering the pH converted cupric oxide to cuprous oxide. 19261

3.2.3, 4.6.1, 3.6.3

Some Properties of Oxide Films Formed during Aqueous Corrosion. J. S. Llewelyn Leach. J. Inst. Metals, **88,** Pt. 1, 24-30 (1959) Sept.

During the aqueous corrosion of certain alloys, sharp changes of corrosion rate are observed. The presence of corrosion-product H has been associated with these effects. Measurements of the electrical capacity and conductivity of the surface oxide layers formed on uranium alloys suggest that the effect of hydrogen is to change the conductivity without altering the thickness of the layer. The relationship between the conductivity and the rate of corrosion is discussed.—BTR. 19287

3.2.3, 6.3.6, 3.7.4

An Electron-Microscopic Study of the Formation of Oxide on Copper Single Crystals Immersed in an Aqueous Solution of Copper Sulphate. G. Tyler Miller, Jr. and Kenneth R. Lawless. J. Electrochem. Soc., **106,** No. 10, 854-860 (1959).

On immersion of a copper crystal in aqueous $CuSO_4$ with pH equal 3.8 an oxide film 20-30 A thick is immediately formed. Some oxide crystals continue to grow rapidly into well-defined polyhedra. Growth spirals were observed on the larger polyhedra after 24 hrs. or more immersion, and after longer periods the pH decreased with subsequent etching of both metal and oxide. The rapid formation and growth of polyhedra is explained on the basis of a supply of copper ions from solution and from the metal, an electrochemical mechanism of reaction, and a dislocation mechanism of crystal growth. 17 references.—MA. 19333

3.2.2, 4.2.1, 3.4.9, 5.4.5

Investigations on Filiform Corrosion of Varnished Steel Plates. (In German.) H. Kaesche. Werkstoffe u. Korrosion, **10,** No. 11, 668-681 (1959) Nov.

Filiform corrosion is a special type of atmospheric corrosion which is mainly encountered on varnished steel sheeting. The attack begins with the formation of drops of electrolyte, e.g., at hygroscopic impurities of the metal surface, and remains strictly limited to the small volume of these drops. The drops which usually have a distinct V-shape, are pushed along on the metal surface below the varnish by solid corrosion products formed there.

The results of tests concerning the dependency of filiform corrosion on the humidity of the air, on the thickness of the varnish, on the nature of polluting salt particles and on the pre-treatment accorded to the steel sheeting lead to the assumption that the salt concentration in the electrolyte drops is in equilibrium with the surrounding atmosphere and that the V-shaped phase boundary, formed by the continually growing rust, constitutes a filter which can only be passed by oxygen. At this filter bivalent iron is oxidized to trivalent iron and is stabilized in V-shape by conditions which are qualitatively governed by the conversion balance of the reaction in the drop and by the surface tension between drop and varnish skin. The speed of the reaction is ultimately governed by the partial pressure of the oxygen in the atmosphere. 19295

3.2.2, 3.7.3, 6.2.5, 3.7.2

Improved Resistance of Stainless Steel Welds to Interganular Corrosion. (In Russian.) G. G. Pocheptsova. Khim. Mashinostroenie, No. 6, 38-40 (1959) Nov./Dec. Translation available from: Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, Calif.

Shortcomings of addition of titanium or columbium to 18-8 stainless steel to improve general and intergranular corrosion resistance. Cause of knife-line attack. Benefits derived from heat treatment (whenever the weldment is not too bulky). Exploration of possibilities of obtaining welds resistant to intergranular corrosion by incorporating into them austenite-forming as well as ferrite-forming elements. Recommended electrode wire composition (increased manganese and aluminum) for maximum resistance to intergranular corrosion.—HB 19399

3.5 Physical and Mechanical Effects

3.5.8, 6.4.2

Stress Corrosion. The Engineer's View. P. H. Wall. J. Royal Aeronautical Soc., **63,** 354-365 (1959) June.

Choice of metals known to be susceptible to stress corrosion. Means for use in design and manufacture to avoid trouble. Aluminum-zinc, aluminum-copper, and other alloys. —BTR. 18588

3.5.8, 3.7.3, 6.2.5

Stress-Corrosion of Austenitic Stainless Steels. (In Japanese.) Masayoshi Tagaya, Hiroshi Imagawa and Deihachi Ishihara. J. Metal Finishing Soc., Japan, **10,** No. 6, 227-232 (1959) June.

Influence of cold drawing, heat treatment, presence of oxidizing agents and cathodic protection on susceptibility to stress corrosion of austenitic stainless steel wires. Boiling 42% magnesium chloride (154C) was used as corrosive solution. The specimens were stressed and time to fracture measured. Effect of heat

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treatment: the specimens which cooled rapidly after heating at 900C in cracked ammonia gas atm. or in air at 1000C were relatively immune to stress corrosion; but the specimens which cooled rapidly after heating at 1150C in cracked ammonia atm., became very susceptible to stress corrosion. Time to fracture for specimens annealed for 1 hr. at 380C after cold drawing is shorter than for "as-cold drawn" specimens. The cold drawn specimens annealed at 650C for 1.5 hrs. showed chromium carbide precipitation, but improved stress corrosion resistance because of stress relief due to heat treatment. Effect of oxidizing agent: when a small quantity of potassium nitrate is added to the corrosive solution, no stress corrosion is noticeable. Effect of cathodic protection: the cathodically protected specimens did not fail for 24 hrs. in the corrosive solution, when the current density exceeded 30μA/cm.^{2} The unprotected specimens failed within one hour. 18647

3.5.4, 6.6.4, 8.4.5

Irradiation of Clad Graphite in High-Temperature High-Pressure CO_2. John C. Smith, William E. Murr, Ward S. Diethorn and William H. Goldthwaite. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-1333, April 7, 1959, 29 pp. Available from Office of Technical Services, Washington 25, D. C.

Graphite specimens fully clad with Type 310 stainless, Type 446 stainless, or Inconel were irradiated in a 1000-psi CO_2 environment for a period of 4 weeks at approximately 1300F followed by 1 week at 1500F. The fast-neutron-plus-gamma dose rate was estimated at 8 x 10^7 rads per hr. The gas environment was sampled and replinished eight times during the experiment. After 60 hours at about 1350F, the carbon monoxide content had increased from a negligible value to 3.6 vol.%. It then decreased steadily to a value of 0.4 vol.% at the end of 4 weeks. When the temperature was raised to 1500F, the carbon monoxide content increased to 1.9 vol.% in 100 hours and then decreased to 0.6 vol.%. The oxygen content remained nearly constant throughout the experiment. Postirradiation examination and metallography revealed very little effect of the exposure on the cladding materials at the gas and graphite interfaces. (auth) —NSA. 18599

4. CORROSIVE ENVIRONMENTS

4.3 Chemicals, Inorganic

4.3.2, 5.9.2, 6.6.8

Resists Hydrochloric and Hydrofluoric, Nitric and Sulfuric Acids. G. Weyermuller and E. M. Kline. Chem. Processing, **22**, No. 6, 126-127 (1959) June.

Since corrosion and other related problems have arisen from handling of fumes from pickling operations in Inco's Huntington Works, company wished to take advantage of experience gained in meeting these problems when planning a new pickling building. In March, 1958, a fume removal system made of glass fiber-reinforced, thermosetting polyester resin was placed in service. Hoods, ducts and stacks were fabricated of this material. Fumes from acid tanks are captured and pulled through side takeoff, slot-type hoods in a balanced air system. Choice of materials and equipment was governed by such factors as initial cost, service life and maintenance. Plastic fume removal system has withstood fumes from acid pickling solutions—which contain various mixtures of hydrochloric acid, hydrofluoric acid, nitric acid and sulfuric acid at temperatures of 125-190 F. There has been no evidence of corrosion and maintenance has been at a minimum. Photos.—INCO. 18641

4.3.7, 3.8.4, 4.2.1, 3.4.3

Reaction Mechanism of the Atmospheric Corrosion of Metals in Humid Air Containing Sulphur Dioxide Contamination. (In German.) K. Barton and E. Beranek. Werkstoffe u. Korrosion, **10**, No. 6, 377-383 (1959) June.

In atmosphere contaminated with sulfur dioxide, course of reaction is often determined by hydrolytic reactions leading to formation of solid reaction products. Reaction mechanisms for formation of corrosion products on iron, aluminum, copper and zinc were determined. Rate of atmospheric corrosion in moist sulfur dioxide-containing atmospheres depends on: concentration of sulfurous acid and sulfuric acid in atmosphere, which determine pH value of adsorbed water-layer; reaction mechanism leading to soluble solid reaction products and physio-chemical properties of these products; rate and reaction mechanism at metal surfaces with adsorbed layers as determined by sulfur dioxide and sulfuric acid; and primary resistance of oxide layers formed in fabrication of metals. Graphs, 14 references.—INCO. 18256

4.3.2, 6.2.5, 6.2.3

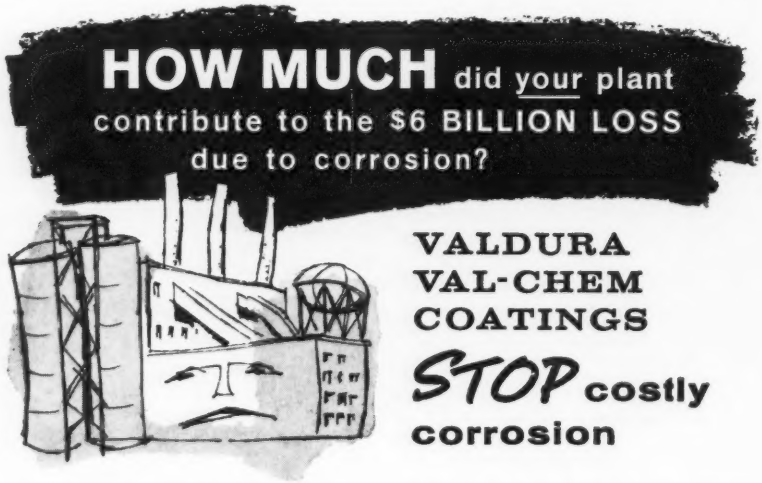
Studies of the Corrosion of AISI 304 Stainless Steel and AISI 4135 Carbon Steel Exposed to Saturated Solutions of Boric Acid. C. R. Bergen—D. D. Whyte, editors. Westinghouse Electric Corp. for Yankee Atomic Electric Co. U. S. Atomic Energy Commission Pubn., YAEC-67, Nov., 1958, 18 pp. Available from Office of Technical Services, Washington, D. C.

AISI 304 stainless steel and AISI 4135 carbon steel specimens were exposed to five wt.% (70F) and thirteen wt.% (140 F) boric acid solutions. These are essentially saturation concentrations. After four weeks exposure it was found that the AISI 304 stainless steel was not attacked under these conditions but that the carbon steel had developed considerable corrosion products in the form of scale. It was found that the attack on carbon steel at 70 F in a five wt.% boric acid solution was greatly reduced by the addition of sufficient base to neutralize the solution. A thirteen wt.% boric acid solution badly attacked the carbon steel at 140 F even when adjusted to neutral pH condition. (auth.) —NSA. 18695

4.3.3, 3.4.3, 6.4.2, 5.8.4

Corrosion Product and Inhibitor Films on Aluminum. H. W. McCune. J. Electrochemical Soc., **106**, No. 1, 63-65 (1959) Jan.

When aluminum corrodes in an alkaline sodium triphosphate solution, phosphate is incorporated into the surface oxide film on the metal. Sodium silicate, potassium permanganate and sodium chromate inhibit triphosphate sorption, especially the first, which has found wide application as an inhibitor in household detergent mixtures containing polyphosphates. In the accompanying table the entries under "$Na_5P_3O_{10}$ deposited" were calculated from the phosphorus-32 activity sorbed on the aluminum specimens which were exposed to uninhibited and inhibited radioactive sodium triphosphate solutions. In electron micro-



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graphs of samples exposed to triphosphate solutions inhibited with sodium silicate there was no evidence of a continuous film covering the surface; evidently the siliceous film is textureless and probably is very thin.—ALL. 17797

4.7 Molten Metals and Fused Compounds

4.7, 6.2.2, 3.2.2, 3.7.4

Formation of a Ternary Carbide During the Attack of Molten Zinc on Iron-Carbon Alloys. Leo J. Hütter and Hans H. Stadelmeier. Z. Metallkunde, **49**, No. 11, 600-601 (1958).

When an Armco iron and a ledeburitic white cast iron containing 4.5% carbon are immersed in molten zinc at 450 C and above, the former shows the ζ, δ_1, and Γ layers, while the latter shows the ζ and δ_1 phases, but no Γ phase, this being replaced by a ternary carbide phase, Fe_2ZnC. This carbide phase, which is embedded in the δ_1 layer, has an ordered f.c.c. lattice with a lattice constant of 3.80 kX.—MA. 18794

4.7., 6.3.10, 8.4.5

Cladding and Structural Materials. Corrosion by Liquid Metals and Fused Salts. J. H. Stang. Reactor Core Materials (Battelle Memorial Inst. Tech. Progress Rev), **2**, No. 1, 30-33 (1959) Feb.

Review article mentioning work done at Brookhaven National Lab., Oak Ridge, Nuclear Development Associates and in Great Britain. Graphs summarize available information on corrosion resistance of various metals, alloys and ceramics to lithium at elevated temperatures (metals include austenitic stainless steels, nickel, Inconel and precious metals; data from Oak Ridge). Although many materials have satisfactory corrosion resistance to lithium in static isothermal systems up to 1500 F, not one checked to date is reistant in dynamic non-isothermal systems. Molten Salt Reactor Program at Oak Ridge includes study to determine corrosion behavior of potentially useful container materials for selected fuel-bearing fluoride salts at 1200 F, with Inconel and INOR-8 of prime interest. Although Inconel has displayed excellent resistance, recent information indicates that resistance of INOR-8 is even better. British reports describe methods of determining oxygen levels in highly purified sodium.—INCO. 18603

4.7, 8.4.5, 6.3.10, 6.2.5

Interim Report on Corrosion by Alkali-Metal Fluorides: Work to May 1, 1953. G. M. Adamson, R. S. Crouse and W. D. Manly. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-2337, June 5, 1959, 36 pp. Available from Office of Technical Services, Washington, D. C.

In connection with the search for container materials suitable for use in high-temperature molten-fluoride reactor systems, the corrosion of several metals by various fused fluoride mixtures was studied in thermal-convection loops made from the metal being tested. In these tests the temperature drop was fairly large, but the velocity of the liquid was low and not subject to control. The fluoride mixture used in most of the study contained 43.5 mole per cent KF, 10.9 mole per cent NaF, 44.5 mole per cent LiF, and 1.1 mole per cent UF_4, and is referred to as "fluoride 14". In a series of screening tests Inconel, or similar high-nickel alloys, was shown to be the most promising container material. The data reported are from loops that were operated for only relatively short times, 500 hr., and with impure fluoride mixtures. The lack of purity of the mixtures was an important consideration in the tests reported. With fluoride 14 an average figure for the maximum microscopically visible attack on Inconel was 0.012 to 0.015 in. after 500 hr. of circulation. The attack was in the form of small voids which did not connect with the surface or with each other. It is shown that for the times used here the attack was caused primarily by the reduction of fuel impurities by chromium metal from the container and by the leaching of sufficient chromium to reach equilibrium concentrations in reactions with the fluorides, primarily with UF_4. In contrast to the effects of impurities, the depth and type of attack varied only slightly when changes were made in the major components of the various fluoride mixtures studied. The only effect definitely established was that, in every case, mixtures containing uranium fluoride caused more attack than did similar mixtures containing no uranium. When the loop was operated at fluid temperature of 1650 F, the attack was slightly deeper than it was at 1300 F. The addition of zirconium hydride to the fuel almost completely eliminated the attack. Alkali metals also acted as inhibitors. It was found that Type 316 stainless steel might be considered for a container for molten fluoride mixtures that do not include potassium fluoride. With such stainless steels and zirconium fluoride-base mixtures, the maximum depth of attack was about the same as that found with Inconel; however, more material was mass-transferred and cold-leg deposits were found. When alkali-metal-base mixtures were circulated in Type 316 stainless steel, plugging occurred in a relatively short time; the plugging was probably caused by the formation of a compound similar to K_3NaCrF_6 (auth.)—NSA. 19610

5. PREVENTIVE MEASURES

5.2 Cathodic Protection

5.2.1, 4.6.11, 1.7.2

Cathodic Protection of Steel Immersed in Sea Water. (In French.) A. Hache. Corrosion et Anticorrosion, **7**, 307-311 (1959) Sept.

Summary of previously published results of work at IRSID's Biarritz corrosion testing station. Projected program for study of cathodic protection. —RML. 19230

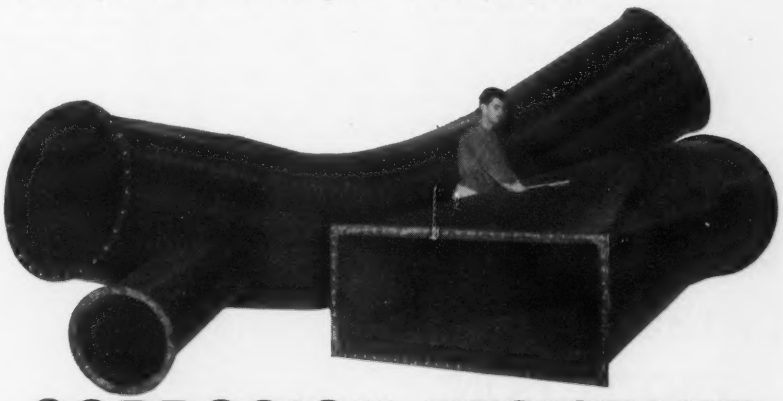
5.2.3, 3.6.9

Advances in Rectifiers Solve Protection Problems. T. R. Stilley. Pipe Line Ind., **10**, No. 3, 51-55 (1959) Mar.

Stray current problem in cathodic protection can be solved by bonding the affected structure to the most negative part of the interfering current. If the interference is variable, half-wave selenium rectifier stacks are effective. Circuit diagrams and calculations for these stacks as well as for silicon diodes are discussed. 18570

5.2.2, 4.6.7, 4.6.11

Electrolytic Manganese as Galvanic Anode in River and Sea Water. Comparison with Zinc Anode. (In Japanese.) Sakae Tajima, Jiro Majima and Takemi Mori. Corrosion Engineering, **8**, No. 10, 415-418 (1959) Oct.



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Behavior of electrolytic manganese (99.95%) as galvanic anode for mild steel sheets in river water (pH 6.6) and in artificial sea water was studied and comparison was made with zinc anode (99.9964%). Corrosion rate of electrolytic manganese in river water was 1.39 mdd. Anode potential of manganese in river water and in sea water was —1.2 ~ —0.75V and —1.3 ~1.1V (S.C.E.) respectively when anode current was held at 0.2 ~ 1mA/cm² at room temperature, using carbon cathode. Manganese anode could protect iron sheets with an area ~ 30 times larger than the area of the manganese anode. Cathode (iron) potential became gradually less noble. Cathode potential after 600 hrs. was —0.8V and 0.04 mA/cm² (river water) and —0.15V and 0.8 mA/cm² (sea water) with a manganese anode, while —0.76 V and 0.01 mA/cm² (river water) and —1.10V and 0.06 mA/cm² (sea water) with a zinc anode.

Manganese galvanic anode had an over all better protective action on mild steel sheets in river water where perfect protection by zinc is difficult, but in sea water, manganese suffered a corrosion of 3800 ~ 4500 mdd i.e. approximately 15 times larger than that of zinc. 18591

5.2.1, 8.9.5

Experiments with a Trailing Platinum Anode. Cathodic Protection of s.s. "Israel" on Haifa-New York Voyage. D. Spector, H. S. Preiser and D. Khoushy. Corrosion Technology, **6,** No. 5, 143-148 (1959).

Advantages of the use of trailing anode systems are enumerated. Details are given of the preparations for the voyage with descriptions of the platinum-clad anode, direct current power source, bow and stern reference electrodes, recording instruments for anode current and hull potential, and propeller shaft grounding brushes. Hull potential/time graphs plotted from data obtained during dock-side tests and three underway runs are given. Methods for overcoming the mechanical difficulties encountered are described. Results indicate the feasibility of protecting cathodically large commercial ships by using inert trailing anodes.—PMR. 1862/

5.2.4, 4.5.3, 8.9.3

Determination of the Amount of Transitional Resistance Between Steel Pipelines and the Ground. (In Russian.) L. Ya. Tsikerman and K. K. Nikol'skii. Gazovaya Prom. (Gas Industry), **4,** No. 3, 40-43 (1959) March.

Necessary cathodic protection for a pipeline is determined based on a formula derived for calculating the resistance to flow of electric current between a pipeline and the ground. The procedure for carrying out the actual measurements varies according to whether they are made on an isolated section of a pipeline or on a portion of a pipeline of infinite length, and whether or not stray currents are present. The circuits to be used in each case are described. 18637

5.2.3

Current and Potential Relations for the Cathodic Protection of Steel in a High Resistivity Environment. W. J. Schwerdtfeger. National Bureau of Standards. J. Research Nat. Bur. Standards, **63C,** No. 1, 37-45 (1959) July-Sept.

Specimens of bare low-carbon steel (cold-drawn tubing) were exposed in laboratory for a period of 2 months to a soil having a resistivity of about 20,000 ohm-centimeter. Previous work in low-resistivity environments by author and by other investigators has shown that corrosion can be reduced to a negligible degree by polarizing a steel structure to —0.85 volt (protective potential) with reference to a copper-copper sulfate electrode. In such studies by author, cathodic polarization curves have also been shown to be useful in indicating current density required for cathodic protection. In present study above criteria were again evaluated. In addition to protecting steel at protective potential (free of IR drop), effect on protection of including IR drop caused by protective current was also noted. Also, cathodic polarization curves were obtained on a recorder in conjunction with a bridge circuit to eliminate IR drop. Results show that best degree of protection was achieved on specimen controlled at —0.77 volt (without IR) with reference to a saturated calomel half-cell. This is approximately equivalent to protective potential —0.85 volt with reference to a copper-copper sulfate electrode. Applied current indicated by break (change-in-slope) in cathodic polarization curve agreed reasonably well with actual current necessary to maintain polarization at —0.77 volt (free of IR). Current required for protection was about 3 times magnitude of corrosion current; therefore, corrosion reaction was either under anodic control (unlike previous studies) or an equivalent type of control which was caused by high resistance at anodic areas. Table, diagrams, graphs, 11 references.—INCO. 18657

5.2.2, 8.9.5

Cathodic Protection of Ships by Magnesium Anodes. (In German.) Anton Schwarz. VDI-Zeitschrift, **101,** 1063-1064 (1959) Aug. 1.

Cylindrical anodes are connected to the ship's hull and surrounded with a thick-walled rubber ring to avoid increase current densities likely to damage the paint protecting the hull.—RML. 18680

5.2.2, 8.9.5

Protection of Double Bottom Tanks. K. G. C. Berkeley. Corrosion Prevention & Control, **5,** No. 7, 43-46 (1958) July.

Experiments on the cathodic protection of double-bottomed cargo tanks with magnesium anodes led to the development of an effective system which is easy to install and has proved effective in 90% of its installations. 18698

5.2.3

Some Platinum Anode Designs for Cathodic Protection of Active Ships. H. S. Preiser and B. H. Tytell. Paper Presented at a Meeting of National Association of Corrosion Engineers' Northeast Region, Boston, Massachusetts, October 6-8, 1958. Corrosion, **15,** No. 11, 596t-600t (1959) Nov.

Voltage-current relationships have been determined for platinum wires, gauze and disc and a platinum-clad tantalum disc, in sea water tests in the laboratory and in Boston harbor.

The platinum-clad tantalum disc produced the best current-voltage ratio. In the range of 5 to 18 volts in the harbor tests, 2.0 amperes were obtained per impressed volt. The other anodes gave 1.3 amperes per impressed volt in the harbor tests. In the laboratory tests, the ratios obtained were 3.2, 3.1, 2.6, 2.2, and 2.1 amperes per volt for the platinum-clad tantalum disc, wire gauze, 48-inch wire spiral, 36-inch wire spiral and the flat disc, respectively. 18133

5.2.1, 8.9.3

Whole System Installed in Nine Months Cathodic Protection of Southern Pacific's High-Pressure Products Pipe Line. D. N. Miller. Corrosion, **15,** No. 2, 104, 106 (1959) Dec.

Various problems encountered and methods used to achieve cathodic protection of a pipe line across central California and Nevada are discussed. Location of rectifiers and anodes used are given. Special problems such as the winter snows, air observation of rectifiers and close proximity to co-axial telephone cable are discussed.

A revision of the paper "Blitzkrieg Cathodic Protection of a High Pressure Products Pipe Line." Presented at the

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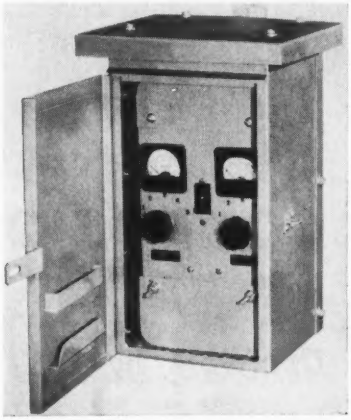

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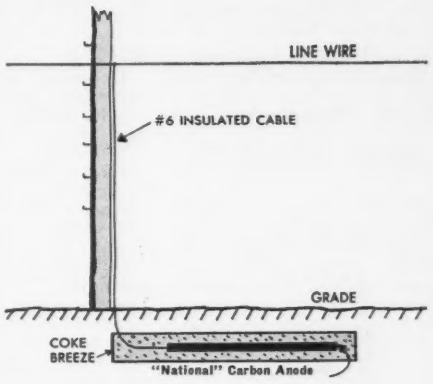

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15th Annual Conference, National Association of Corrosion Engineers, Chicago, March 16-20, 1959. 18111

5.2.1, 5.4.5, 4.6.7, 7.4.2

Cathodic Protection of Coiled Tube Cooler Immersed in High Resistivity Fresh Water. (In Japanese.) Toshiichi Hikozawa and Masaaki Hanada. Corrosion Engineering, **8,** No. 9, 370-372 (1959) Sept.

Comparison test of cathodic protection on coiled tube type intercoolers, immersed in high resistivity fresh water was done by applying, (1) galvoline anodes, (2) impressed current system using steel bar anodes, (3) zinc rich paint coating, (4) combined system of (2) and (3); the last system was found to be the best. 18730

5.3 Metallic Coatings

5.3.2, 5.3.4

Resistance to Corrosion of Aluminum-Coated Steel Wire. E. T. Englehart and K. J. Brondyke. Symposium on Aluminizing, Wire Association Annual Convention, Atlantic City, New Jersey, October, 1958. Wire and Wire Products, **33,** No. 11, 1365-1367, 1370-1372, 1404-1405 (1958).

Hot-dip coating is reviewed. Aluminum-coated steel is preferred to galvanized steel since the two metals are electrochemically neutral; aluminum alloy wire is preferred to either aluminum-coated steel wire or galvanized steel-core wire in resistance to corrosion. —MA. 18022

5.3.2

Molybdenum Coatings. H. W. Schultze, R. R. Freeman and J. Z. Briggs. Am. Metal Climax, Inc. Materials in Design Eng., **49,** No. 1, 76-81 (1959) Jan.

Status report on properties and uses of molybdenum coatings, and how they are applied. Physical properties, adhesion, hardness, ductility, strength, wear resistance and corrosion resistance are considered. Commercial and experimental applications in electronic components, automotive equipment, aircraft, armament and nuclear reactors (e.g. electrophoretic coatings on Inconel shafts, and molybdenum coatings on graphite and stainless steel to make them impermeable to hydrogen and other gases) are discussed. Table summarizes commercially available coatings, those in advanced development stage, and those in laboratory development stage and includes ceramic metallizing, metal spraying, electrophoretic deposition, vapor deposition, electrodeposition, sputtering and vacuum evaporation. Photos.—INCO. 18675

5.3.4

Chromium Plating in Relation to the Corrosion Resistance of Nickel-Chromium Deposits. A. Smart. Electroplating and Metal Finishing, **12,** No. 1, 3-10 (1959) Jan.

Author summarizes work carried out by British Non-Ferrous Metals Research Assoc. in England and by Udylite Corp. and others (including W. A. Wesley and B. B. Knapp, Inco) in U. S. A., which shows that corrosion problems perplexing so many users of nickel and chromium plated components exposed to outdoor atmosphere conditions are not due to deficiencies in nickel plate, but that they can be eliminated by control of chromium plating conditions and thickness of chromium deposit which is used. Porosity and crack pattern of chromium plate, optimum chromium plate, and effect of physical condition of nickel, are discussed. Ideal conditions involve coating thickness approaching 80 micro inches, temperature of 130 F, current density of 300 amp/sq. ft., and sulfate ratio in region of 150:1 to 200:1, but very significant improvement over present-day practice can be achieved by operating at 120-125 F, sulfate ratio of 125:1 or 150:1 and current density, of 200 amp/sq. ft. to produce chromium deposit of 40 micro inches thick. Excellent outdoor corrosion results can be obtained with this chromium coating over 1 mil deposit of bright nickel. Photomicrographs.—INCO. 18665

5.3.4

Metal Spraying in Relation to the Corrosion Process. J. R. Franklin. Corrosion Technology, **5,** No. 10, 323-325 (1958) October.

Deals with function of metal spraying in prevention of corrosion. When steel structure is sprayed with aluminum or zinc, principle of protection is cathodic protection; zinc or aluminum coating becomes sacrificial anode. Protection is proportional to weight and thickness of sprayed coating. Application equipment and metal surface preparation are discussed. Table gives metallizing speed and coating weight for aluminum, Sprabronze AA, Monel, Ni, Metcoloy I (18-8), Metcoloy II (high-C, high Cr stainless), Sn, and Zn.—INCO. 18791

5.3.2, 6.3.9, 7.1, 4.2.3

Evaluation of Protective Coatings for Molybdenum Nozzle Guide Vanes. Period covered January 1954 to July 1957. John R. Giancola. U. S. Wright Air Development Center, Technical Note 58-241, Feb. 10, 1958, 45 pp. Available from: Wright-Air Development Center. Materials Lab., Wright-Patterson AFB, Ohio.

Thirty seven molybdenum nozzle guide vanes coated for resistance to jet engine operating conditions were evaluated in an engine exhaust stream at 1860-1890 F for 4 hours. Non-destructive and metallographic examinations revealed the degree of deterioration of each type of coating after test. Results indicate that, in the temperature range of the test, multilayer electrodeposited metallic coatings have the longest service life. No one coating combination survived the test without some serious damage. All coatings tested increased the life of the guide vanes over unprotected molybdenum. (auth)—NSA. 18767

5.3.4

Kinetics of Cathodic Processes During Electrodeposition of Metals. (In Russian.) A. V. Izmailov. Nauch. Doklady Vysshei Shkoly. Khim. i Khim. Tekhnol. (Scientific Proceedings of the Higher School-Chemistry and Chemical Technology, No. 2, 240-244 (1958). Chem. Absts., **52,** No. 21, 18016 (1958) Nov. 10.

Relation between the effective activation energy (A) of the electrode process and ΔE are given graphically for a series of electrolytes, from which the value A_η (the activation energy for concentration polarization) is found. The nature of the cathodic polarization was studied and was found, for most investigated electrolytes, to be of a concentration character. Measured values of viscosity (η) and heat conductivity (k) of various solutions of electrolytes are given for different temperatures together with the calculated values of A. In electroplating baths, in which the structure and stability of the complexes and the solvate

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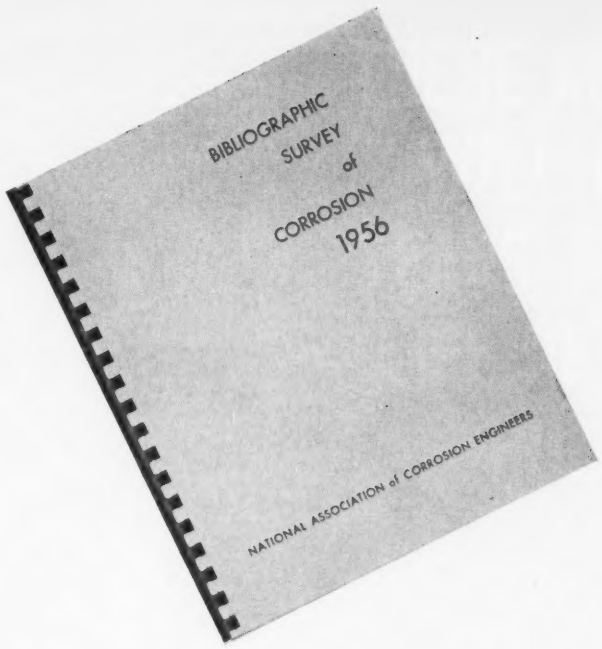

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compounds forming the electrolyte vary, a significant rise in temperature, in order to increase the production of these baths, is not recommended, since the quality of the resulting coatings is not as good. On the contrary, the structure of the complex ions does not vary much with increasing temperature in the case of cyanide electrolytes for copper, silver, zinc and cadmium plating and consequently a rise in temperature does not affect the quality of the deposits.—MA. 18803

5.3.4, 5.4.5

Sacrificial Metals as a Base for Organic Coatings. K. Tator. Ind. and Eng. Chem., **50,** No. 8, 77A-78A (1958).

Examples are quoted which demonstrate that it is more economical (bearing in mind the subsequent durability) to apply to steel a sacrificial metal coat followed by an organic coating than to use either alone. Suitable sacrificial coats may be sprayed aluminum or zinc, zinc applied by galvanization or zinc-rich paints. Good results were obtained with vinyl resin coatings applied over the last two.—RPI. 19593

5.3.4

Chromized Steel—A New Low Cost, Heat, Wear or Corrosion Resistant Material. R. P. Seelig. Paper before Soc. Automotive Engrs., Nat'l. Passenger Car, Body & Materials Mtg., Detroit, March 4-6, 1958. SAE Journal, **66,** No. 5, 42-44 (1958).

By means of the Chromalloy process, ordinary iron and steel can be made to resist rusting like stainless steel, or resist wear and abrasion like tungsten carbide and be protected against oxidation similar to high alloy materials. Chromalloy process, or Chromallizing, is a patented method of diffusing Cr and other elements into the surface of metal. As Cr diffuses into base metal it combines with elements therein to form an alloy case which is an integral part of base metal, but with properties of the new alloy. Unlike superficial coatings, the case won't peel, spall, chip or flake off. Stainless steels, Ni or Co base alloys, W, Mo and other metals can be Chromallized to provide protection from oxidation and erosion at very high temperatures—up to 3000 F. Photos.—INCO. 19479

5.3.4

Applications of Composite Electrochemical Materials. J. A. Edwards. Product Finishing (London), **12,** No. 1, 66-69 (1959).

A note on the C.E.M. processes for the deposition of composite coatings consisting of nickel, cobalt, nickel/cobalt/copper, iron, brass, chromium, cadmium, silver, gold, platinum and zinc with additions of Al_2O_3, SiC, WC, and etc.—MA. 19764

5.3.4, 6.4.2

Electroless Nickel Plating of Aluminium. L. Bosdorf and K. Müller. Aluminium, **35,** No. 7, 391-393 (1959).

Various methods, embodying an interlayer of another metal such as zinc, are reviewed from the literature.—MA. 19702

5.4 Non-Metallic Coatings and Paints

5.4.5, 4.6.6

Tests on Underwater Paints, Particularly for Drinking-Water Tanks. G. Sille and O. Damm. Die Technik, **14,** 39 + 4 pp. (1959) Jan.

The tests showed that a chlorinated polyvinyl chloride gives much better protection against corrosion than a bitumen. When the former is used for drinking-water tanks the usual plasticizer, tricresyl phosphate, must be replaced by dibutyl phthalate and chlorinated diphenyl, to prevent contamination of the water with traces of phenols.—RPI. 19467

5.4.5

High Build Epoxy Resin Maintenance Finishes. G. R. Somerville. Paint Ind. Mag., **74,** No. 8, 6 + 4 pp. (1959).

The use of cold-cured epoxy resin mastics and epoxy resin/coal tar mastics to give high-build coatings for the protection of plant in highly corrosive areas is outlined. Sprayable epoxy resin compositions containing no volatile material are also described.—RPI. 19490

5.4.8, 3.5.9

Paints and Varnishes Resistant to High and Low Temperatures. (In French.) J. L. Rabaté. Travaux Peintures, **14,** No. 7, 264-269 (1959).

Conditions under which paints are likely to be required to resist high or low temperature are described. For the high-temperature paints, the resistance of the pigment as well as the medium is considered and for low-temperature paints the particular problem of painting steel and zinc surfaces in refrigerating rooms is discussed.—RPI. 19413

5.4.5

Some Experiences with Lead Pigments in Corrosion Resistant Paints. Paint Manufacture, **29,** 130-131 (1959) April.

Calcium plumbate has many useful attributes as a component part of anticorrosive paints. In some circumstances and for some applications, red lead pigment still gives the best results.—B I R. 19382

5.4.5, 5.4.6, 5.5.1

Paints, Preservatives and Coatings. T. B. Owen. Paper before Armed Forces Chem. Assoc., 14th Annual Mtg., Washington, Sept. 10-11, 1959. Armed Forces Chem. J., **13,** No. 6, 22-23, 33 (1959) Nov.-Dec.

Reviews Navy's requirements for protective coatings, covering types of paints and paint failures, general and special performance requirements (ice resistance, antifouling), rust preventives (liquid and solid), strippable coatings, boiler preservation, hydraulic systems, ballast tank coatings and wood preservation.—INCO. 19373

5.4.5

Which Vinyl Coating Process for Metal Parts? F. J. Nagel. Prod. Eng., **30,** No. 27, 70-72 (1959). Brit. Plastics Fed. Absts., **14,** No. 9, 801 (1959).

Four methods are given for coating metals with vinyl resins and the choice of method for any particular application is discussed. The thickness range, thickness uniformity, edge coverage, appearance, substrate shape and coating cost for each is considered.—RPI. 19360

5.4.5, 5.9.1

Corrosion Prevention Through Proper Surface Preparation and Use of Epoxies. W. C. Naumann. Paint Ind. Mag., **74,** No. 3, 12 + 4 pp. (1959).

Surface preparation, proper application of the various paint coats and the selection of the correct coating materials for the environment involved are factors considered in the use of epoxy resins in corrosion-resistant maintenance finishes.—RPI. 19354

5.4.2, 6.2.3, 3.5.9

For High Temperature Protection—New Ceramic Coatings. Nuclear Energy Engr., **13,** 448-449, 454 (1959) Sept.

The compositions are given of promising coatings to be used in the protection of low-carbon steel at temperatures up to 1200 F. Frits, in which various oxides were substituted for B_2O_3, were designed and smelted. The most successful oxides were $Zn_3(PO_4)_2$ and $Ca_3(PO_4)_2$. Coatings which contain cerium oxide or both cerium oxide and chromic oxide as a refractory addition show the best results.—NSA. 19344

5.4.5

New Urethane Coatings: Tops in Resistance. R. B. Norden. Chem. Eng., **66,** No. 3, 144, 146, 148 (1959) Feb. 9.

Urethane coating is produced by polymerization between polyfunctional isocyanates and resins containing hydroxyl groups. Compared with vinyls, urethanes are more resistant to alkalis and solvents; as good against acids and water; better in heat durability, abrasion and wear resistance. Major classes of urethane coatings are described, and their properties and applications discussed. Table rates their corrosion resistance to a number of corrosives.—INCO. 19342

5.4.5

Pigment Aid Against Corrosion. H. H. Muirhead. Paint J., **9,** Nos. 72, 73, 765 + 3 pp., 50 + 2 pp. (1959).

The use of lead cyanamide in protective coatings is reviewed. Antisettling and brushing properties are good, as are resistance to heat, impact and abrasion and rapid through drying is obtained. The high alkalinity of the pigment is claimed to last over several years.—RPI. 19328

5.4.5

Behaviour of Anticorrosive Paints in Relation to Their Composition. (In French.) P. Marpon. Peintures, Pigments, Vernis, **35,** No. 6, 311-317 (1959).

Protection against corrosion depends on physical and chemical processes. Various anticorrosive pigments, their use in primers for ferrous structures and medium and surface factors generally are considered.—RPI. 19308

5.4.2, 6.4.2

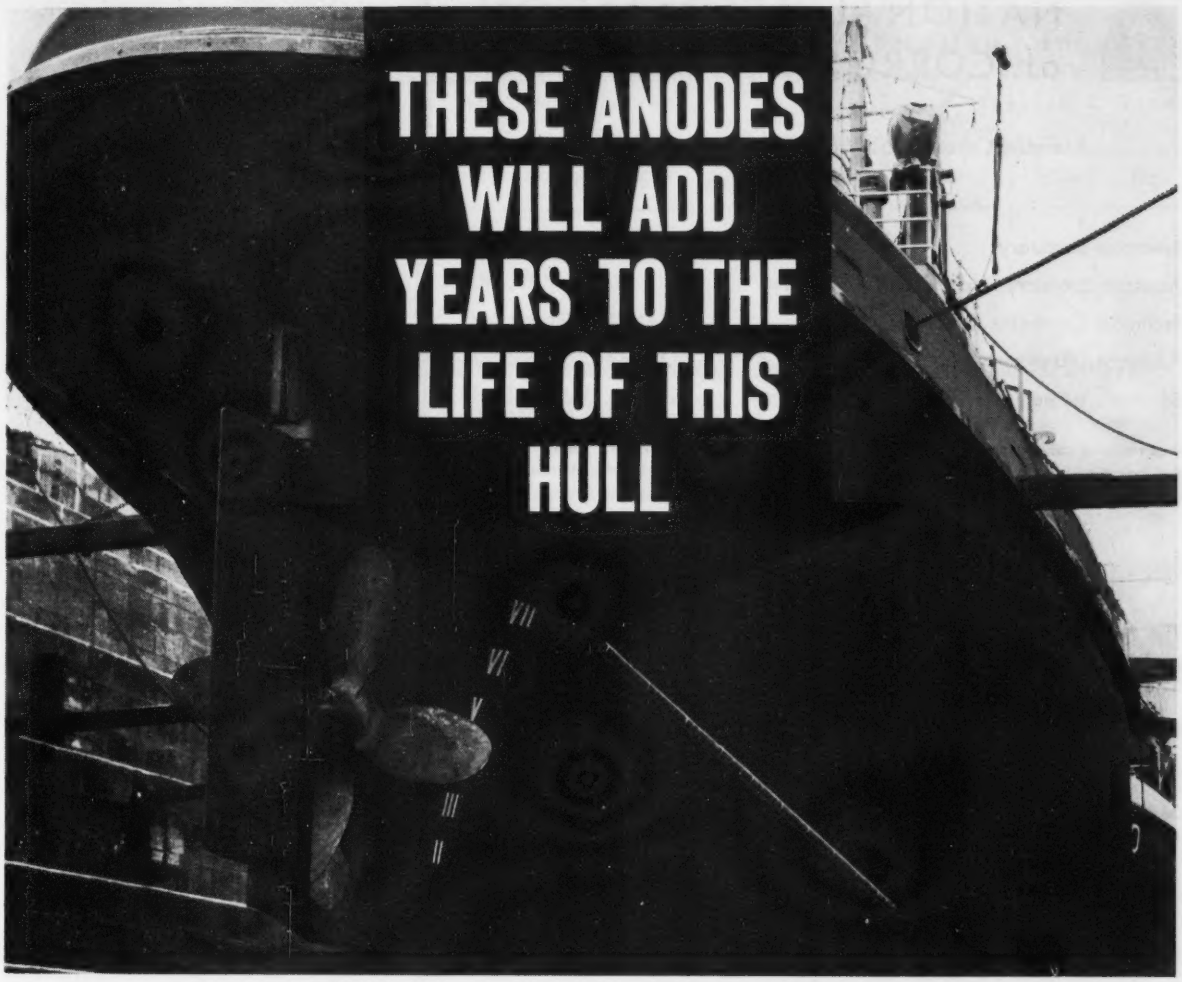
The Development of Vitreous Finishes for Aluminium. L. Lister and T. E. V. Stephenson. Light Metals, **22,** No. 254, 156-157 (1959).

Lister and Stephenson compare the properties of standard American frits containing lead with two recently developed British frits, one lead-bearing and the other lead-free. Abrasion resistance, scratch resistance, chemical stability (both acid and alkali), and atmospheric corrosion of the fired articles were measured mainly to the credit of the British frits. All are fired at 560-580 C without an undercoat, after suitable surface-treatment.—MA. 19291

5.4.2, 3.5.9

Ceramic Coatings for Insulation. Alan V. Levy. Metal Progress, **75,** No. 3, 86-89 (1959).

The properties of flame-sprayed and phosphate-bonded coatings of aluminum oxide and zirconium dioxide and those reinforced by metal strip or mesh are given. They are resistant to temperature up to 4000 F. (2200 C.)—MA. 19294



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OFFICIAL MONTHLY PUBLICATION

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An Association of Individuals and Organizations Concerned with Control of Corrosion

1061 M & M Building Houston 2, Texas

Vol. 17 March, 1961 No. 3

Topic of the Month

Tin Plated Cans Sprayed With Soluble Oil Formulation Show Increased Rust Resistance*

By RAYMOND K. COHEN*

Abstract

An SRI soluble oil formulation was developed for the treatment of cans. The formulation was an emulsion of a soluble oil in water containing sodium nitrite inhibitor and a surface active agent (Deriphat 151). Cannery trials indicated this spray treatment gave satisfactory results at a cost of less than one cent per case of canned goods. 5.5.1, 7.5.1, 8.3.5

Introduction

EXTERNAL CORROSION can be a problem when cold canned goods are moved into a warm, humid environment. A means of reducing this corrosion problem was developed in the course of a recent research program carried out by Stanford Research Institute on the evaluation and control of sweat damage. This research program dealt with the specific problem of damage resulting from shipment of canned goods by sea from West Coast ports.

It was found that corrosion of the tin plate could be reduced by subjecting the cans to a special treatment just prior to application of the labels. Passing the cans through a spray chamber resulted in a very thin film of protective material being deposited on the surface of the cans.

Many different materials were investigated for their effectiveness in preventing corrosion. A suitable material, in addition to reducing corrosion, must also be nontoxic, cause no interference with the labelling operation, and have no effect upon the shiny appearance of the tin plate. Furthermore, the material should be one which can be safely applied in the cannery without danger of fire or explosion, or any harmful effect upon the health of the operating personnel. Finally, the material must be low enough in cost to make its application economically feasible.

Soluble Oil Formulation

The study resulted in development of an SRI soluble oil formulation for the treatment of cans. This formulation is an emulsion of a soluble oil in water and contains an inorganic corrosion inhibitor (sodium nitrite) and a surface active agent (Deriphat 151). The latter acts as a wetting agent and also contributes to the rust-inhibiting characteristics of the film deposited on the can. Most favorable concentrations of the various components were found to be: 5 to 20 percent of the soluble oil, 0.5 to 2 percent of the corrosion inhibitor, and 0.25 to 5 percent of the surface active agent. Cannery trials indicated the cost of this protective material to be less than one cent per case of canned goods. Figure 1 shows a prototype of the spray machine in operation during a cannery trial run.

The protective treatment was found to be quite effective under relatively light exposure conditions. As the severity of the exposure increases, the effectiveness starts to break down. Thus, in the case of the ocean transport problem, severe condensation conditions may necessitate the use of other control measures to supplement the protective treatment of the cans.

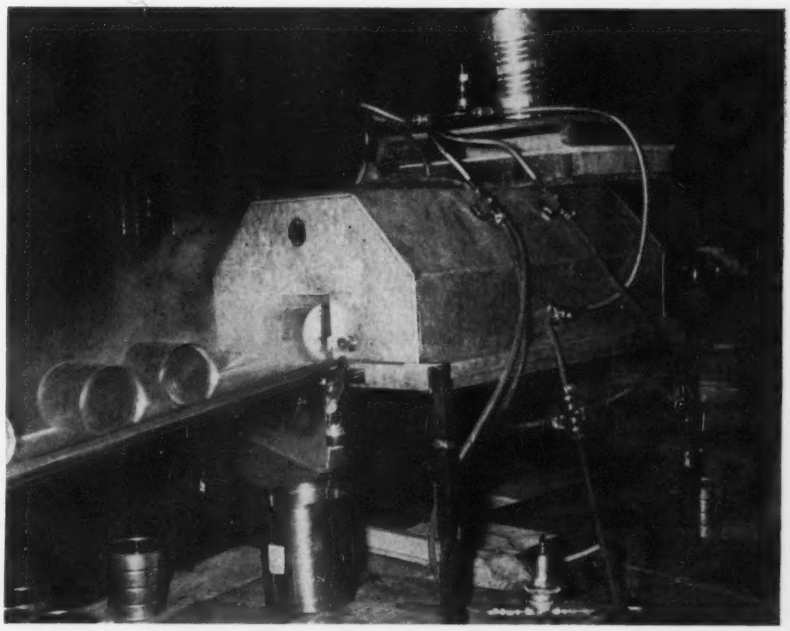

Figure 1—Prototype of spray machine in operation during a cannery trial run.

★ Submitted for publication August 1, 1960.

* Chemical engineer. Physical and Biological Sciences Division, Stanford Research Institute, Menlo Park, California.

Corrosion of Reinforcing Steel in Concrete In Marine Atmospheres*

By HOWARD F. FINLEY

Abstract

A brief review is given of the corrosion of reinforcing steel in concrete structures exposed to sea water action. The relations of concrete porosity, permeability, strength, water-saturation, and electrical resistivity to the corrosive action are discussed. It is postulated that the existence of macro-galvanic cells in concrete structures are chiefly the result of differential oxygen concentrations in the pore space water. The differences in oxygen concentrations arise from differing oxygen solubilities in pore space water of different concentrations of dissolved sea salts and from lower availability of oxygen in those areas of high water-saturation. The corrosion of the reinforcing steel found in the San Mateo-Hayward bridge is used to illustrate the corrosion mechanism. Recommendations are given for preventing corrosion in new structures and for correcting the problem in existing structures. 6.6.5, 4.6.11, 3.6.2

Introduction

THE USE OF reinforced concrete structures in coastal areas is not always successful. Many times the reinforcing steel corrodes, the corrosion products occupy more space than did the steel and excessive internal pressures build up. The concrete then cracks or spalls from the reinforcing bar, and there is an attendant loss of structural strength.

Figures 1, 2, and 3 show a typical example of this type of failure. These pictures are of an abandoned 26 year old platform in Lake Maracaibo, Venezuela. Had the platform been in use the structural members would have been repaired before reaching this advanced degree of deterioration.

A survey[1] was made in 1916 of numerous concrete structures along the seaboard of the United States. It was found that the majority of all reinforced-concrete structures on the American coasts subject to sea-water action showed evidences of deterioration or failure due to the corrosion of the embedded reinforcement above the water line. The conclusions of this survey were:

1. The corrosion occurs first followed by the cracking. There were few, if any, cases of structural failure caused by corrosion of the reinforcing steel at the base of a crack.

2. Corrosion occurs only above the water line and then only where the concrete is exposed to salt spray.

3. A large concentration of accumulated sea salts invariably was found in concrete with corroded reinforcing bar.

4. The corrosion of the reinforcing bar was not related to chemical deterioration of the concrete.

The status of the knowledge of the corrosion of reinforcing steel in concrete structures exposed to sea-water is much the same today. It has been shown by a number of investigators and recently in a most convincing way by Tremper, Beaton, and Stratfull[2,3,4] that the corrosion is galvanic and that macro-galvanic cells exist with the corroded area anodic and separated by as much as several feet from the cathodic area.

Although corrosion of reinforcing steel is widespread it is known that concrete can be made that will prevent this from occurring. Various authors[5,6] have pointed out very old concrete structures in sea-water that are as sound today as the day they were placed. The differences between structures in which corrosion is found and those in which it is absent are not always immediately apparent. It is the purpose of this paper to discuss the physical properties of concrete and the variables that must be considered in explaining the corrosion of reinforcing steel.

★ Submitted for publication May 9, 1960.

About the Author

HOWARD F. FINLEY is supervisor of the Corrosion Section of the Production Department of Creole Petroleum Corporation, Cabimas, Estado Azul, Venezuela. His principal interests are cathodic protection and process corrosion. He received a PhD degree from the University of Texas where he did research on the fundamental properties of polar organic corrosion inhibitors. He is a members of NACE, ACS, and The Society of Petroleum Engineers.

Physical Properties of Concrete

Concrete is composed of sand, gravel, crushed rock, or other aggregates mixed with hydraulic cement and water. The cement is a mixture of complex calcium silicates and aluminates which hydrate with the water to form a solid hardened mass containing entrapped the sand and aggregate. These last two components are essentially inert; it is the quality of the hardened cement that most influences the corrosion of reinforcing steel.

The physical properties of hardened cement pastes have been thoroughly studied by Powers and Brownyard.[7] For purposes of discussing corrosion of reinforcing steel only the final stages of hydration are important where the cement particles are nearly 100 percent hydrated. In this stage the paste consists of a solid cellular mass that has a considerable amount of free space. This free space is filled with air and with water containing dissolved solids. The paste is permeable to the passage of air and water and has a fairly high electrical resistivity.

Porosity

Porosity is defined as that fraction of the bulk volume of concrete that is not occupied by solid framework. It represents the percentage of the total space that is available for occupancy by either gases or liquids. Powers and Brownyard[8] concluded that in cement pastes there are two types of pores: (1) gel pores (i.e., small pores between the gel particles within the paste), and (2) capillary pores (i.e., larger pores that exist between aggregates of gel particles). In concrete, in addition to these, there are relatively large pores that form beneath aggregate particles due to the settling rate of the cement particles being faster than that of the aggregate. Equations for both gel and capillary porosity are given by Copeland and Hayes.[9] The total porosity is proportional to the water-cement ratio.

Permeability

Permeability is a measure of a porous material's capacity to transmit fluids through its interconnected pore network. If the pores of the medium are not interconnected there can be no permeability; hence there is a relationship between permeability and effective porosity but not between permeability and absolute porosity. It will be shown in this paper that permeability is the single most important physical characteristic of concrete that influences the corrosion of reinforcing steel.

Permeability is determined by measuring the flow of a fluid through a sample under a given pressure gradient and is expressed by the Darcy's Law Equation:

$$K = \frac{Q\mu L}{\Delta P A} \qquad (1)$$

where K is the permeability in darcys, Q the rate of flow of the fluid in cubic centimeters per second, μ the fluid viscosity in centipoises, L the length of the sample in centimeters, ΔP the pressure differential in atmospheres, and A

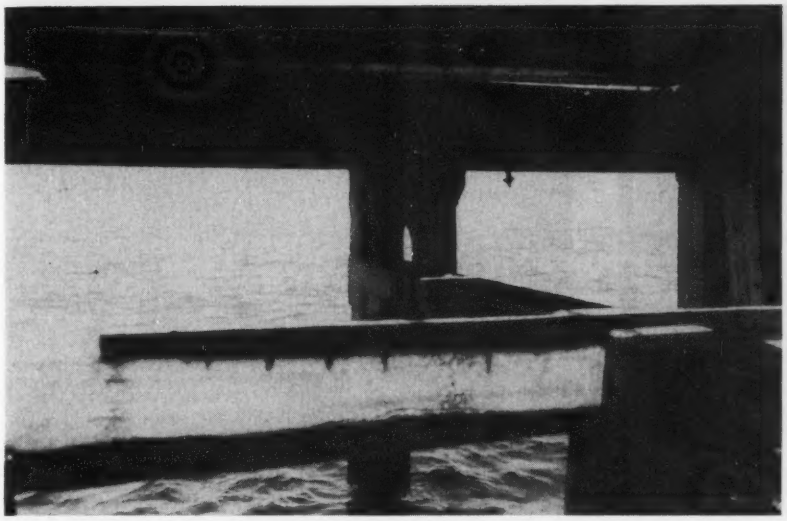

Figure 1—Underside of a 26 year-old Lake Maracaibo platform showing structural deterioration due to corrosion of reinforcing steel.

the cross-sectional area of the sample in square centimeters. For convenience the millidarcy, one one-thousandth the darcy, is used.

Permeability is related to other properties of the material by the Kozeny equation:

$$K = \frac{\phi^3}{2t^2 S_v^2 (1-\phi)^3} \times 10^8 \qquad (2)$$

where ϕ is the effective porosity, t the tortuosity of the interconnected pore channels, and S_v the specific surface of the solid framework of the paste.

Powers and Brownyard[10] solved equation (2) in terms of the water-cement ratio, evaporable water, void space, non-evaporable water, and a factor proportional to the specific surface of the hydrated cement particles. Using their result they calculated the permeabilities of cement pastes from the data of Ruettgers, Vidal, and Wing,[11] and found that the calculated values were much lower than those determined experimentally, the discrepancy becoming greater the greater the water-cement ratio. With high water-cement ratios, discontinuities develop during the bleeding period that allow permeating water or air to bypass the regular pore network. Concretes show a much greater than theoretical permeability due to fissures that form under aggregate particles as the paste settles faster than the aggregate.

Powers and Brownyard[12] estimated the minimum permeability of a well cured paste of low water-cement ratio to be about 2.5×10^{-6} mds. Other authors[13, 14, 15] have reported obtaining permeabilities of 8.3×10^{-8} mds to 2.2×10^{-1} mds. The permeabilities of cores taken from the Lake Maracaibo platform shown in Figures 1, 2, and 3 averaged 4.7 mds. The ratio of these permeabilities is over fifty million indicating the difference of concrete found in practice.

For concrete, during the bleeding period the cement particles settle faster than do the aggregate particles and voids are left beneath the latter. In addition air bubbles rise through the fluid mix and become entrapped beneath the aggregate particles. These suggest that the shape and size of aggregate influences the permeability. The Bureau of Reclamation Concrete Manual[16] shows this to be the case for coarse aggregate. Carlson[14] demonstrated that lean mixes with a sand fineness modulus of 2.25 gave a permeability only 42 percent that of a mix with a fineness modulus of 2.50. The use of smaller size aggregate and fine sand definitely lowers the permeability. However, this is somewhat offset by the increase in permeability due to the additional water required to maintain a given workability.

The method of curing also influences permeability. Powers, Copeland, Hayes, and Mann[13] found that curing a specimen at 79 percent relative humidity increased its permeability seventy-fold as compared to specimens properly cured.

The permeabilities given in this section were liquid permeabilities determined on core samples fully saturated with water. The permeability of a porous substance to any fluid is maximum when the pores are saturated with that fluid. When the pores are filled with more than one immiscible fluid the permeability to either fluid is less than if the structure were 100 percent saturated with that fluid. The permeability depends on the fluid saturation and will be greater the greater the saturation. The permeability to air in a 100 percent water-saturated concrete structure is zero.

Strength

The compressive strengths of hydrated cement pastes have been shown by Powers and Brownyard[17] to be a linear function of the gel-space ratio; that is the ratio of the volume of the hydrated gel to the original space available. For the pastes studied they gave the equation:

$$S = 120{,}000 \frac{V_m}{w_o} - 3600 \qquad (3)$$

where S is the compressive strength in psi, V_m the volume of water required to form a monolayer on the solid particles and w_o the original water content or the original space available.

The important factor in equation (3) is not the actual strength but that the strength is directly proportional to the surface area of the solid phase. Equation (2) showed that the permeability is inversely proportional to the square of the surface area. The higher the strength of concrete the lower is its permeability.

An increase in strength of concrete through hydration represents a corresponding decrease in permeability. Concrete completely submerged continuously gains in strength for its entire life. Wakeman, Dockweiler, Stover, and Whiteneck[5] reported a 1-year strength of 3615 psi and a 20 year strength of 5305 psi for continuously submerged samples. The average 28 day strengths for a group of neat cement cylinders was 3890 psi. After being submerged in Lake Maracaibo for 1 year the strengths had increased to 6720 psi. It seems fairly certain that the continuously submerged parts of coastal structures are more highly hydrated than those parts above water and consequently have a lower permeability.

Water-saturation

The pore space (both gel and capillary) of hydrated cement is usually considered to consist of a water solution of calcium hydroxide, sodium hydroxide, potassium hydroxide, and possibly other dissolved hydration products. The water in concrete exists in two forms: (1) non-evaporable—that which is adsorbed on the surface of the cement particles and may be considered as part of the solid, and (2) evaporable—that which may be evaporated depending on the relative humidity of the atmosphere in contact with the concrete. Water-saturation (σ) refers to the second of these. Concrete may experience any degree of water-saturation from 0 to 100 percent. Its value will be 100 percent only when the surface of the concrete is in contact with liquid water. Those parts of a marine structure above the water line have water-saturations less than 100 percent, but the saturation probably approaches 100 percent near the water line.

Dissolved Oxygen

At any degree of water saturation less than 100 percent the void space of concrete contains water, water vapor, and air. In permeable concrete the air may diffuse a considerable distance into the mass of the structure. The water in contact with the air is saturated with oxygen, its total oxygen content depending on its dissolved solids content and the solubility of oxygen. There will be a higher dissolved oxygen concentration in those areas of the concrete of a sufficiently low water-saturation to permit diffusion of air into the pore space and whose capillary water has a lower dissolved solids content.

Electrical Resistivity

The electrical resistivity of concrete

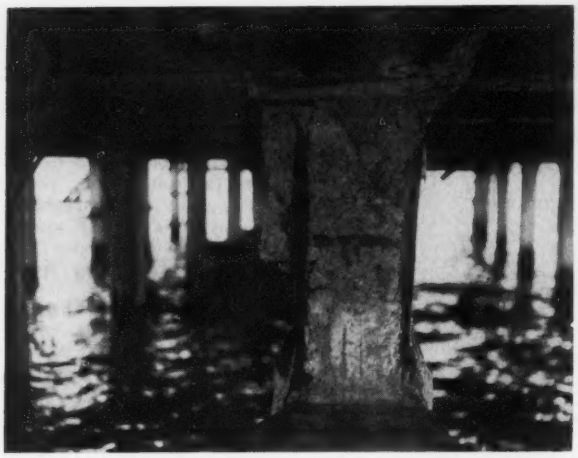

Figure 2—Pile showing exposed corroded reinforcing steel.

Figure 3—Underside of floor showing exposed corroded reinforcing steel and cracks in floor and pile.

is determined by its total evaporable water content (total porosity and degree of water saturation) and the resistivity of the pore space water which in turn is determined by its dissolved solids content. An empirical equation used in oil reservoir engineering to relate porosity, water saturation, and resistivity is

$$R_t = \left(\frac{1}{\sigma}\right)^2 R_w \phi^{-m} \qquad (4)$$

where R_t is the true resistivity of a formation rock, σ the water saturation, R_w the resistivity of the formation water, ϕ the porosity, and m a constant depending on the degree of consolidation of the rock. A similar relation probably holds for concrete. High concrete resistivity is favored by a low porosity, a low water saturation, and a pore space water of high resistivity.

Corrosion of Reinforcing Steel

The San Mateo-Hayward Bridge

In order to relate the variables discussed above to the corrosion of reinforcing steel in a structure exposed to a salt water environment, a specific case will be considered. Gewertz, Trempter, Beaton, and Stratfull have made a thorough study of the severe corrosion of reinforcing steel in the San Mateo-Hayward Bridge in the San Francisco Bay area. For a complete account of their findings the reader is referred to their four excellent papers.[2, 3, 4, 18] A brief summary of what the writer considers their most significant results is given below.

1. The corrosion was in the form of deep pits.

2. No corrosion was found below the water line.

3. There was no relation between the corrosion of the reinforcing steel and either prior cracking of the concrete or chemical deterioration of the concrete.

4. The concrete in the corroded area was highly permeable. It was of low strength, its strength apparently having retrogressed from a higher value.

5. Considerable quantities of absorbed sea salts were found, especially in the areas of greatest corrosion. There was a gradual decrease in salt content progressing inward from the surface of the concrete, indicating that the salt had accumulated from spray or splashing. The greatest amount of salts was found in the area between mean tide and the highest level of spray action.

6. Potential profiles showed that the areas where there was corrosion were anodic to areas where there was no corrosion. The anodes and cathodes were separated by as much as 10 feet.

7. Repairs made by chipping out the corroded areas, applying shot-crete in extra thickness, and then applying an asphalt coating increased the severity of the corrosion under the coating.

8. Later repairs made by chipping out the corroded areas and applying shot-crete (without the asphalt) often caused the old anodic area, now covered with shot-crete, to become cathodic to the area around it.

9. The deterioration of the concrete was greater the lower its electrical resistivity. The resistivities in the cathodic areas were greater than in the anodic areas.

Mechanism of the Corrosion

Stratfull[3, 4] has explained the corrosion of this reinforcing steel as being due to unequal concentrations of sea salts which produced corrosion cells of the differential concentration type. Lewis and Copenhagen[19] after an extensive study of the corrosion of reinforcing steel in concrete structures in South Africa concluded that the corrosion was due to unequal salt concentrations that resulted from unequal permeabilities in the concrete. They noted that oxygen was necessary to promote the corrosion.

The fact that oxygen is necessary in the corrosion mechanism in concrete seems obvious from the type of failure always reported. The steel corrodes, producing a corrosion product of greater volume than the steel consumed in the reaction. This corrosion product literally has no place to go so that it produces large internal pressures in the structure and cracks the concrete. In a rigid mass such as concrete it is difficult to see how this increase in volume could occur unless atoms migrate in from the outside. This is most easily explained by diffusion of oxygen. It is doubtful that there has ever been a case of seriously corroded reinforcing steel in concrete sufficiently impermeable to prohibit access of oxygen to the steel (except, of course, cases of stray-current corrosion).

That the chloride ion or other dissolved salts are not necessary to the corrosion mechanism is proven by at least one failure where salts were not involved. Shermer[20] reported typical corrosion of reinforcing steel in a lumber drying kiln where the concrete was exposed to warm moist air. The concrete was of fair quality, testing between 3000 and 4000 psi but there was little cover over the steel. Shermer reasoned that in order to facilitate casting the small beams a high water-cement ratio was used producing permeable concrete.

The facts accumulated to this point suggest that the primary cause of the corrosion of reinforcing steel in permeable concrete and the establishment of widely separated anodes and cathodes is differential oxygen concentration. The differential oxygen concentrations arise in two ways: (1) there is a difference in the solubility of oxygen in solutions of different dissolved solids content and (2) there is a greater availability of oxygen in those areas of lower water-saturation due to a higher permeability to air. The following mechanism is proposed.

In the spray and splash zone of concrete structures, sea water is deposited on the surface of the concrete in varying amounts. The amount deposited depends on such physical features as relative location of structural members, wave action, prevailing wind direction, and wind force. The water either adheres to the surface, runs off, or evaporates depending on the relative humidity, exposure to sun and wind, inclination of

the surface to the horizontal, and height above the water line. The concrete will absorb water, its ultimate saturation depending on how wet its surface is maintained.

The water that evaporates will leave sea salts behind. Their distribution on the surface of the concrete will be unequal. The salts diffuse by capillary action into the pore space of the concrete. The dissolved salt content of the pore space water increases in proportion to the amount of salt that was deposited on the surface and will not be the same throughout a member. Increasing salt content decreases the solubility of oxygen. Since the water-saturation of the concrete, except near the water line, is less than 100 percent, the concrete is permeable to air. Air diffuses into the pores and oxygen dissolves in the capillary water, the oxygen concentration being greater where the salt content and water-saturation are lower. Galvanic cells arise with the anodic areas either high salt/low oxygen or high water-saturation/low oxygen and the cathodic areas low salt/high oxygen or low water-saturation/high oxygen.

To illustrate the effect of dissolved salts, the chloride content of a cored sample from the platform shown in Figures 1, 2, and 3 was 13,135 ppm based on the air dried weight of the core. The porosity fraction was 0.147. If the pore space is considered to have been filled with water and the salt as sodium chloride is considered all to have been dissolved in the pore space water, then there were approximately 33 grams of sodium chloride for each 100 grams of water. The solubility of sodium chloride in pure water at 35 C (ambient temperature of Lake Maracaibo) is 36.4 grams per 100 grams water. When it is considered that there were other dissolved solids in the pore space water the water was undoubtedly saturated with lake salts.

Uhlig[21] gives the solubility of oxygen in water in equilibrium with air saturated with water vapor at 30 C as being 7.67 ml/l at zero chlorinity and 5.37 ml/l at a chlorinity of 20,000 ppm. At 330,000 ppm it is even less.

The differential aeration cells in concrete are much the same as those found on pipe lines alternately passing through dry and marshy areas. Potential differences[22] of 0.5 to 0.9 volts have been found and result from the higher oxygen concentrations in dry porous sands as compared to water-logged sands, the wet areas being the anodes. Stratfull[3] found potential differences on the order of 0.5 volts in the San Mateo-Hayward bridge.

The results obtained in applying the two different methods of repair to the San Mateo-Hayward Bridge corroborate differential oxygen concentration as being the primary cause of the corrosion. When shotcrete and asphalt were applied the deterioration proceeded at a faster rate than it had before. Covering the area with asphalt retarded the diffusion of oxygen to the reinforcing steel and this area continued anodic to other parts of the structure. The use of shotcrete without asphalt produced the exactly opposite effect. The fresh shotcrete had not accumulated any sea salt, the solubility of oxygen in the pore space water was relatively high, and the area became cathodic to the other parts of the structure that had an appreciable salt content.

In the progress report on the protective methods being applied to the bridge, Stratfull[4] discussed wetting units used to keep the surface of parts of the bridge continuously wet with water. It is interesting to note that the ratio of anodic to cathodic area increased from 1-to-15 to 1-to-4 in six months. The concrete wet with water was fully saturated, its permeability to air was zero, the supply of oxygen to the reinforcing steel was restricted, and additional anodic area developed.

Lewis and Copenhagen[19] pictured the corrosion of reinforcing steel as resulting from a cell of the type:

Steel (Anode)	Permeable Concrete	Less Permeable Concrete	Steel (Cathode)
	low pH	high pH	
	high Cl^-	lower Cl^-	
	high O_2	lower O_2	

They reason that the driving force of the corrosion cell is the difference in chloride content coupled with the difference in pH and that the differential oxygen cell is of less importance and opposes the primary cell. This is equivalent to saying that the differential oxygen cell is providing a measure of corrosion protection. Their representation of the cell implies that the different salt contents and dissolved oxygen concentrations are due solely to differences in permeability. Anodic and cathodic areas are usually separated from each other by 2 to 10 feet. It appears doubtful that significantly different permeabilities would be found that close together in a single structural member. Powers, Copeland, Hayes, and Mann[13] found that cement pastes of the same water-cement ratio are likely to have similar permeabilities after they have reached fairly advanced stages of hydration. It is more likely that the differences in salt content are due to different spray and splash action than to significantly different permeabilities.

Other Effects of Sea Salts

The presence of sea salts influences the corrosion of reinforcing steel in ways other than its effect on oxygen solubility. At very high concentrations it reduces resistivity; hence anodic areas caused by high salt content are always of lower resistivity permitting increased galvanic currents. The presence of salts both lowers the pH of the pore space water and raises the pH required to protect the steel. Shalon and Raphael[23] showed that 30 percent sea salt lowered the pH of a saturated calcium hydroxide solution from about 12.6 to 11.7 and that whereas in calcium hydroxide solutions no corrosion was observed above pH 12, with 3.6 percent sodium chloride, corrosion was observed to pH 12.6. The chloride ion is an anodic depolarizer and increases corrosion currents by its depolarizing action. However in the absence of oxygen it is doubtful that appreciable corrosion currents are produced.

Absence of Corrosion of Reinforcing Steel Below the Water Line

If differential oxygen concentration is the cause of the corrosion of reinforcing steel, at first analysis it would be expected that the worst corrosion should occur below the water line. This area is fully water saturated and its oxygen content can be considered to be zero. However no corrosion occurs. This in no way invalidates differential oxygen concentration as being the principal cause of the corrosion of reinforcing steel. The reactions possible at the surface of steel in an area of low oxygen concentration are different from those in an area of no oxygen. The absence of oxygen in submerged parts of structures probably permits the establishment of a highly protective film that prevents ferrous ions from passing into solution. This film is in little danger of undermining by chloride ion penetration since the pore space water has only limited access to chloride ions.

Thus in the highly alkaline environment of concrete, differential aeration cells that produce corrosion exist between areas of high oxygen and low oxygen but not between areas of high oxygen and no oxygen. A similar situation is found with bare steel flowlines in Lake Maracaibo. Typical differential aeration corrosion is found on the riser with the water line area cathodic to the lower part of the riser. The corrosion rate decreases somewhat as the distance from the surface increases. There is a sharp increase in corrosion rate at the elbow where the horizontal enters the mud. There is active corrosion in the first 1 to 2 inches of the bottom. One of the reasons for the higher corrosion rate here is the differential aeration cell between the low but real concentration of oxygen in the first inch or so of the bottom and the higher concentration of oxygen in the water. At a greater depth where there is no oxygen there is no corrosion.

Prevention of the Corrosion of Reinforcing Steel in Concrete Structures

Corrosion of reinforcing steel in concrete structures can be prevented by producing impermeable concrete. This has long been recognized in the industry. Unfortunately, what constitutes impermeable concrete has not been specified. There are no provisions for using permeability measurements as a criteria for specifications. It is probably not necessary to go to such great lengths since the permeability can be inferred from other variables such as strength and water-cement ratio but the permeability should not be neglected in design considerations.

The permeability of 4.7 mds. is obviously unacceptable since the Lake Maracaibo structure having this permeability was seriously deteriorated. The permeability of 8.3×10^{-8} mds. reported

by Powers, Copeland, Hayes, and Mann[13] is the lowest found in the literature. Somewhere between lies a value that is sufficiently low to prevent corrosion but not so low that it is impractical to attain. Further tests are required to state a range of permeability that should not be exceeded. For now all that can be said is that concrete for marine exposure should be batched with as high a cement content and low a water-cement ratio as is practicable.

Specific Mix Recommendations

For pilings or other parts of a structure exposed to spray or splash action, 7½ bags of cement per cubic yard are recommended with 5 gallons of water maximum per bag of cement. The water content should be reduced to a lower value if workability permits. The aggregates should be washed with fresh water. As much of the structure as practicable should be precast. To insure maximum consolidation, the concrete should be placed by vibration. Precast members should be cured at least 14 days with water prior to installation. Cast-in-place members should be well cured with water or a commercial curing compound. The use of 2 inch cover seems adequate but 2½ inches would be a hedge against poor workmanship. The entire placing and erection operations should be rigorously inspected to insure that all specifications are met.

For those parts of coastal structures that are not directly subjected to spray or splash, seven bags of cement per cubic yard are sufficient. For spun prestressed piles, eight bags should be used. The aggregate should be well graded to prevent undue segregation during the spinning process.

Arresting Corrosion in Existing Structures

Arresting the corrosion of reinforcing bar in an existing structure is a more difficult feat to accomplish. That the corrosion exists implies that the concrete is porous and permeable, has accumulated sea salts in unequal concentrations and has a low resistivity. Any measure which further reduces the oxygen available to the anodic areas increases the corrosion of those areas and any measure which increases the oxygen availability stands the chance of diverting the corrosion to areas previously cathodic. One method of stopping all corrosion would be to insulate the entire structure against the diffusion of air. This could be done by completely covering the structure with an air-impermeable coating or by using wetting units and saturating the concrete with water. The first seems the more practical of the two. A 10 or 12 mil coating of a thin film plastic paint over the entire structure should stop corrosion. Covering only the anodic areas would intensify corrosion.

A third method which appears to be the most practical is cathodic protection. The initial results of Stratfull[4] look promising. Future progress reports on this project should establish the feasibility of using cathodic protection.

Conclusions

The physical properties of hardened concrete that affect the corrosion of reinforcing steel were discussed. It was postulated that permeability is the principal physical characteristic influencing the corrosion. The corrosion was attributed to differential oxygen cells that arise due to differing oxygen solubility in pore space water of unequal dissolved solids content and to restricted availability of oxygen in areas of high water-saturation. Recommendations were made for preventing corrosion in new structures. Arresting corrosion in existing structures can probably be accomplished with thin film plastic coatings or with cathodic protection.

Acknowledgment

Permission of Creole Petroleum Corporation to publish this paper is acknowledged. Helpful discussions were held with R. L. Benedict, G. J. Grove, and C. H. Luther of Creole Petroleum Corporation and Dr. S. P. Ewing of Jersey Production Research Laboratories.

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Editor's Note: A paper by H. K. Cook entitled "Concrete for Sea Water Exposure with Particular Reference to Piling"[23] may be of interest to our readers. It appeared in *Corrosion*, 8, 247 (1952) July.

ADDENDUM

Since the writing and review of this paper, Schaschl and Marsh* have shown that in complex differential aeration-differential salt cells all of the corrosion of the anode is accounted for by the differential aeration cell. In the split cells used the cell current was independent of salt concentration provided there was sufficient conductivity in each zone to prevent resistance control. Although the salt contents varied widely (0.2 percent vs 3 percent) there was no external cell current when there was no differential oxygen and there was little local action current when there was no oxygen. The cell currents were very sensitive to scale formation on the anode. Complex pH-differential aeration cells were also studied. There was no discussion of cells with pH greater than 9 but the authors promised a future publication that possibly will take up this pH region and shed light on the lack of corrosion in submerged structures.

* E. Schaschl and G. A. Marsh. *Corrosion*, 16, No. No. 9. 461-467 (1960) September.

Any discussion of this article not published above will appear in June, 1961 issue.

Hydrogen Pickup During Aqueous Corrosion Of Zirconium Alloys*

By WARREN E. BERRY, DALE A. VAUGHAN and EARL L. WHITE

Abstract

Hydrogen absorption during the corrosion of zirconium alloys has been studied in 600 and 680 F water and 750 F 1500-psi steam. Results on binary sponge-base alloy series indicate that, of the alloying elements found in Zircaloy-2, nickel at increasing levels markedly increases hydrogen absorption. Tin has little or no effect, while iron and chromium additions reduce hydrogen absorption. Antimony additions also reduce hydrogen absorption. However, additions of arsenic, antimony, bismuth, or tellurium to Zircaloy-2 do not affect the amount of hydrogen absorbed during corrosion. It is postulated that in zirconium alloys containing iron, chromium, or nickel the compounds of these elements are cathodic to the zirconium matrix. The resulting potential difference is sufficiently high to anodically polarize the zirconium and thus improve corrosion resistance. Apparently iron and chromium compounds readily depolarize hydrogen and thereby decrease the possibility of its passage through the oxide film. Nickel compounds probably do not depolarize hydrogen and may aid in its passage through the oxide film.

6.3.20, 4.6.1, 3.7.2, 3.2.2

Introduction

THE MECHANISM and means of reducing hydrogen absorption in zirconium alloys during exposure in pressurized-water reactors is currently receiving a critical review because of new demands in design requirements. Alloys exhibiting high strength at elevated temperatures over extended periods are needed. The principal use for zirconium has been as a fuel-element cladding material. Embrittlement of the zirconium from hydrogen could result in cladding rupture and exposure of the less corrosion resistant nuclear fuel to the primary coolant water. A serious consequence would be the transport of radioactive fission fragments to all portions of the reactor circuit. If the fuel alloy were not corrosion resistant, a catastrophic meltdown might occur because of lack of heat transfer and blockage of coolant passages from the corrosion product buildup and swelling of the fuel element.

There are several sources of hydrogen in a pressurized-water reactor. Hydrogen is intentionally added to the coolant water to combine with free oxygen which may be present from the radiolytic decomposition of the water. Water is formed, rather than the oxygen reacting with nitrogen under irradiation to form nitric acid. The latter could result in corrosive effects on reactor components.

The radiolytic decomposition of water also is a source of hydrogen. However, excessive quantities do not build up because of the recombination of hydrogen and oxygen to form water. Corrosion of the cladding also is a source of hydrogen which, because of its ionic or atomic form and its proximity to the metal surface, can be very effective in hydriding zirconium. It is this latter source of hydrogen which will be considered in this paper.

There has been considerable work performed in studying the variables which influence hydrogen absorption in zirconium alloys during corrosion in high-temperature water. It has been demonstrated that dissolved hydrogen in the water is not responsible for severe hydriding of Zircaloy-2.[1,2] Gaseous hydriding ceases upon the introduction of water vapor. Zirconium with an oxide film from exposure to high temperature water does not hydride readily upon exposure to gaseous hydrogen at temperatures of interest (680 F).[1,2,3] A partial pressure of 30 atmospheres of hydrogen has not resulted in excessive hydriding of Zircaloy-2 in 750 F 1500-psi steam.[1]

It has been found that the amount of hydrogen absorbed in Zircaloy-2 ranges from 15 to 50 percent of that theoretically available from the corrosion reaction.[1,4,5] Comparison-type corrosion tests have shown that this percentage remains unchanged with either time of exposure, pH in the range of 6 to 10, or during irradiation.[5,6]

Other studies have shown that nickel and platinum additions result in increased hydrogen absorption in zirconium under cathodic polarization during exposure to high-temperature water.[7] A similar effect has been observed with nickel additions to Zircaloy-2.[6] Hydrogen absorption in these nickel alloys is increased during corrosion in the presence of irradiation or with dissolved hydrogen in the water.[6] The effect of nickel in increasing hydrogen absorption will be further demonstrated in this paper. In addition, it will be shown that binary additions of antimony, chromium, and iron to sponge zirconium reduce hydrogen absorption during corrosion. Finally, results will be presented for tests with alloys containing antimony, arsenic, bismuth, or tellurium additions to Zircaloy-2. The basis for these studies was related to the low overvoltage of nickel and its ability to catalyze hydrogenation reactions. Sulfur and other elements are known to poison the catalytic effects of nickel in chemical reactions. Thus the elements described above were added in the hope that a similar effect might be exerted on the nickel in zirconium alloys.

Experimental Procedures

The effect of individual alloying elements on hydrogen absorption was studied in binary sponge-base zirconium alloys.

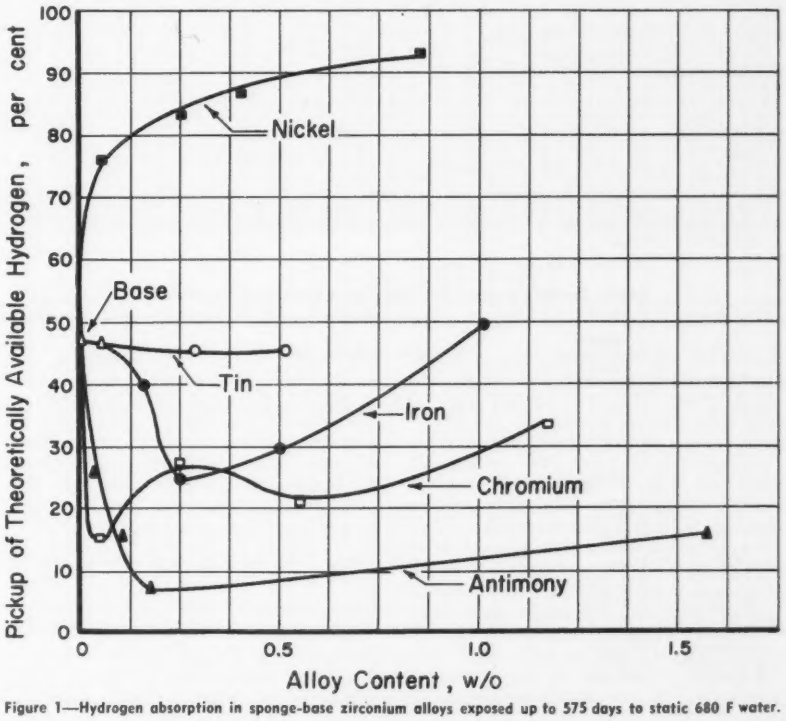

Figure 1—Hydrogen absorption in sponge-base zirconium alloys exposed up to 575 days to static 680 F water.

★ Submitted for publication August 12, 1960.

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TABLE 1—Sponge-base Zirconium Alloys Exposed to Static 680 F Water

Alloy Addition, Weight Percent	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed		
			PPM	mg per dm²	Percent of Theoretical
Unalloyed*	168	146	215	8.6	46
Zircaloy-2	406	112	107	8.1	58
0.29 Sn	126	118	177	6.7	45
0.51 Sn	112	147	189	8.4	45
0.16 Fe	532	118	128	5.9	39
0.24 Fe	392	113	77	3.5	24
0.50 Fe	392	117	114	4.3	29
1.07 Fe	392	127	180	7.9	49
0.05 Cr	126	134	60	2.5	15
0.24 Cr	112	111	80	3.8	27
0.55 Cr	70	153	96	3.9	20
1.30 Cr	168	136	130	5.8	34
0.06 Ni	574	113	276	11.1	77
0.25 Ni	574	139	319	14.3	81
0.41 Ni	574	109	322	11.8	85
0.85 Ni	518	118	350	13.9	94
1.8 Ni	168	Lost Weight	550	21.5	..
0.03 Sb	308	112	50	3.6	26
0.10 Sb	364	107	29	2.1	15
0.17 Sb	210	145	25	1.4	8
1.57 Sb	364	118	45	2.3	15

* Base alloy contained 0.100 weight percent oxygen, 0.045 weight percent iron, 0.006 weight percent nitrogen, 0.005 weight percent nickel, 0.005 weight percent tin, 0.004 weight percent chromium, and 0.002 weight percent hydrogen.

TABLE 2—Analyses of Zircaloy Heats Prepared for Program

Base Material	Nominal Additions, Weight Percent	Analysis (Balance Zirconium), Weight Percent							
		Sn	Fe	Cr	Ni	As	Sb	Bi	Te
Zircaloy-2	None	1.60	0.17	0.10	0.05	<0.001	<0.001	<0.0001	<0.02
	0.07 Sb	...	...	...	...	.....	0.05	.....	....
	0.20 Sb	...	...	...	...	.....	0.20	.....	....
	0.50 Sb	...	...	...	...	.....	0.41	.....	....
	1.0 Sb, 0.5 Ni	...	...	...	0.45	.....	1.0	.....	....
	0.15 As	...	...	...	...	0.03	.....	.....	....
	0.15 Te	...	...	...	...	.....	.....	.....	0.14
	0.15 Bi	...	...	...	...	.....	.....	0.11	....
Modified Zircaloy-2 (1 weight percent Sn)	None	1.05	0.12	0.10	0.03	<0.001	<0.001	<0.0001	<0.02
	0.07 Sb	...	...	...	...	.....	0.05	.....	....
	0.20 Sb	...	...	...	...	.....	0.14	.....	....
	0.50 Sb	...	...	...	...	.....	0.46	.....	....
Modified Zircaloy-2 (0.25 weight percent Sn)	None	0.31	0.24	0.11	0.04	<0.001	<0.001	<0.0001	<0.02
	0.07 Sb	...	...	...	...	.....	0.06	.....	....
	0.20 Sb	...	...	...	...	.....	0.17	.....	....
	0.50 Sb	...	...	...	...	.....	0.51	.....	....

The effects of nickel on hydrogen absorption and alloying to overcome the adverse effects of nickel were studied in Zircaloy-2 and modified Zircaloy-2 containing 0.25 and 1.0 weight percent tin.

The binary sponge-base alloys were available from a previous study (sponge metal is produced by reduction of zirconium chloride by calcium, magnesium, or sodium). They had been vacuum-arc melted in a rocking-hearth furnace (tungsten electrode), and then fabricated at 1370 to 1530 F. They were subsequently vacuum annealed at 1440 F in argon. (Available analyses for these alloys are presented with the corrosion results in Table 1.)

The Zircaloy-2-type alloys were prepared by consumable-electrode arc melting. A single ingot of Zircaloy-2 served as melting stock for the series of Zircaloy-2 alloys. The modified Zircaloys were prepared by adding the prescribed elements to sponge zirconium. All alloys were melted twice. Analyses obtained for the Zircaloy heats are presented in Table 2.

Specimens were shaper finished after annealing to a rectangular cross section shape. Total surface area was 6 to 10 sq. cm. Specimens were then pickled for 3 minutes in a room-temperature solution of 50 volume percent water, 45 volume percent concentrated HNO_3, and 5 volume percent HF. They were then rinsed overnight in cold water. Finally the specimens were measured and weighed before insertion in the autoclave.

Vacuum-fusion analyses for hydrogen were made on the as-pickled specimens for initial content and on selected specimens after corrosion testing.

Corrosion tests were conducted in static, 1-liter AISI Type 316 stainless steel autoclaves. Corrosion specimens were suspended from wire hooks and were not electrically insulated from the autoclave since previous experience at Battelle had indicated that insulation was not necessary.

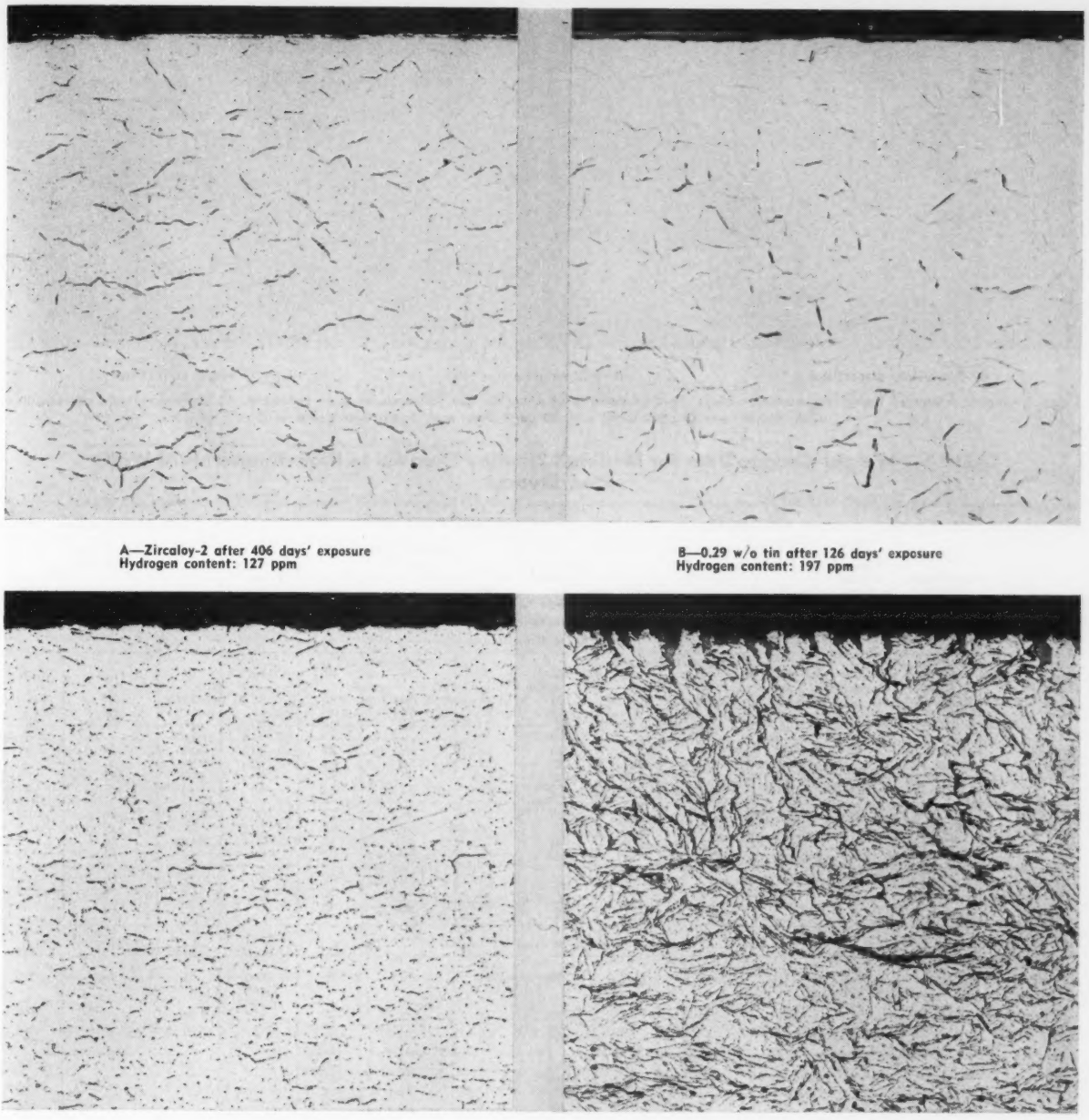
Specimens were exposed to water at 600 and 680 F and to steam at 750 F and 1500 psi. Tests were conducted under degassed conditions and under a 2-atmosphere partial pressure of hydrogen. The 2-atmosphere pressure of hydrogen was applied externally to the autoclave and was transmitted to the autoclave headspace by means of palladium tubing. The end of the tubing within the autoclave was seal welded. The other end was open and extended to the outside of the autoclave through a brazed seal. Analysis of the water indicated that the hydrogen partial pressure within the autoclave was about ⅔ atmosphere.

Specimens were examined after total exposure times of 7, 14, and 28 days and every 28 days thereafter. Autoclaves were refilled with fresh water at the beginning of each exposure period.

Results

Binary Alloys

The effect of alloy additions on hydrogen pickup was studied on binary-alloy series of sponge-base zirconium containing antimony, chromium, iron, nickel, and tin which had been exposed to static



A—Zircaloy-2 after 406 days' exposure
Hydrogen content: 127 ppm

B—0.29 w/o tin after 126 days' exposure
Hydrogen content: 197 ppm

C—0.50 w/o iron after 392 days' exposure
Hydrogen content: 134 ppm

D—1.8 w/o nickel after 168 days' exposure
Hydrogen content: 570 ppm

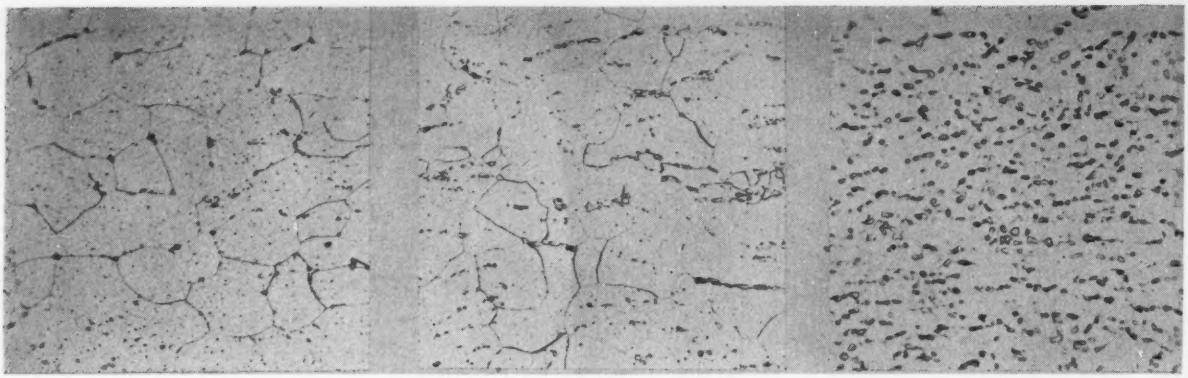
Figure 2—Appearance of hydride needles in sponge-base zirconium alloys exposed to static 680 F degassed water. All photomicrographs approximately 120X; etchant was 30 parts lactic acid, 30 parts nitric acid, 1 part hydrofluoric acid.

680 F water for times ranging up to 574 days. Sponge zirconium and Zircaloy-2 also were included in the investigation for comparison purposes. All specimens were exposed well beyond the transition in corrosion rates, and almost all exhibited total weight gains of approximately 125 mg per dm^2. The corrosion films appeared to be adherent on all specimens except a 1.8 weight percent nickel alloy. Hydrogen analyses before corrosion testing were not secured for the alloys, but were presumed to be about equal to the 20-ppm content of the sponge base.

The weight gains and hydrogen pickup after corrosion for the alloy series are presented in Table 1. The results indicate that the binary alloys containing up to 0.85 weight percent nickel were the most corrosion resistant, followed in order by Zircaloy-2, the iron alloys, and the antimony alloys. The chromium and tin alloys were less resistant than the base.

The amount of hydrogen absorbed as compared with that liberated during the corrosion reaction also is shown in Table 1. If it is assumed that all of the hydrogen pickup by an individual specimen is a result of corrosion, it is apparent that sponge zirconium and Zircaloy-2 absorbed as much as 58 percent of the theoretically available hydrogen, while the nickel alloys absorbed a higher percentage of the corrosion hydrogen than the other alloys.

The percentage of theoretical hydrogen absorbed is plotted in Figure 1 as a function of alloy content. The high percentages for the nickel alloys are quite striking. Even the 0.06 weight percent nickel alloy absorbed about 75 percent of the hydrogen from corrosion. The tin alloys behaved much like the sponge zirconium. Antimony, chromium, and iron alloys exhibited a minimum in theoretical hydrogen pickup at very low alloy levels. The minima were well below the percentage of theoretical pickup for the sponge zirconium.



A—0.16 weight percent iron B—0.24 weight percent iron C—1.07 weight percent iron

Figure 3—Microstructures of sponge zirconium-iron alloys. Note precipitates of zirconium-iron compounds at grain boundaries. All photomicrographs approximately 400X; etchant was 30 parts lactic acid, 30 parts nitric acid, 1 part hydrofluoric acid.

TABLE 3—Weight-Change Data for Modified Zircaloy Exposed to High-Temperature Water and Steam*

Alloy	Addition, Weight Percent	600 F Water				680 F Water				750 F 1500 PSI—Steam			
		Time to Transition, Days	Weight Gain, mg per dm²			Time to Transition, Days	Weight Gain, mg per dm²			Time to Transition, Days	Weight Gain, mg per dm²		
			14 Days	Transition	224 Days		14 Days	Transition	224 Days		14 Days	Transition	224 Days
Degassed Conditions													
Zircaloy-2 (1.6 Sn)	<0.001 Sb	No Transition	12	....	33	125	21	38	61	110	21	50	107
	0.05 Sb	"	13	....	32	125	21	59	83	85	24	56	125
	0.20 Sb	"	14	....	36	110	27	44	80	95	24	60	151
	0.41 Sb	"	15	....	31	110	20	43	88	120	26	73	281
Modified Zircaloy-2 (1.05 Sn)	<0.001 Sb	"	12	....	39	85	18	39	73	65	23	40	87
	0.05 Sb	"	14	....	43	130	36	56	83	75	21	44	93
	0.14 Sb	"	15	....	50	110	44	65	94	90	23	49	93
	0.46 Sb	"	13	....	36	110	24	48	71	85	24	53	161
Modified Zircaloy-2 (0.31 Sn)	<0.001 Sb	"	12	....	61	95	20	48	77	100	23	46	80
	0.06 Sb	"	13	....	44	115	16	39	65	70	21	39	79
	0.17 Sb	"	17	....	62	120	24	48	67	100	23	46	76
	0.51 Sb	"	12	....	34	120	18	39	67	65	22	47	140
Zircaloy-2 (1.6 Sn)	0.03 As	"	24	....	33	115	24	50	92	85	25	62	161
	0.14 Te	"	14	....	47	105	38	53	86	80	24	56	132
	0.11 Bi	"	16	....	48	125	38	60	88	95	25	62	127
2 Atmospheres of Hydrogen													
Zircaloy-2 1.6 Sn)	<0.001 Sb	Not Determined	18	....	37	110	19	26	75	Not Determined	26	..	93
	0.05 Sb	"	26	....	45	110	18	28	73	"	26	..	170
	0.20 Sb	"	31	....	49	105	22	33	88	"	27	..	216
	0.41 Sb	"	33	....	49	95	21	30	117	"	45	..	283
Modified Zircaloy-2 (1.05 Sn)	<0.001 Sb	"	31	....	53	135	19	30	72	"	28	..	98
	0.05 Sb	"	28	....	48	125	18	29	69	"	28	..	117
	0.14 Sb	"	29	....	52	110	17	32	75	"	29	..	156
	0.46 Sb	"	24	....	40	105	16	30	72	"	41	..	173
Modified Zircaloy-2 (0.31 Sn)	<0.001 Sb	"	40	....	71	120	14	28	78	"	25	..	82
	0.06 Sb	"	31	....	63	120	13	30	80	"	20	..	87
	0.17 Sb	"	44	....	72	115	15	29	82	"	28	..	99
	0.51 Sb	"	16	....	37	120	15	33	83	"	26	..	117
Zircaloy-2 (1.6 Sn)	0.03 As	"	27	....	42	95	16	30	91	"	29	..	181
	0.14 Te	"	31	....	47	100	16	28	74	"	..	Not Tested	...
	0.11 Bi	"	38	....	57	100	16	29	102	"	26	..	195

* Obtained from log-log plot of weight gain-time data.

Examples of the microstructures of the corrosion-tested binary zirconium alloys are shown in Figure 2. The microstructures of the sponge-base and the chromium and low-antimony alloys were similar to that of the tin alloy shown in Figure 2. The darker hydride needles were uniformly dispersed throughout the specimens and, in most instances, were located at grain boundaries. Note the high concentration of needles in the 1.8 weight percent nickel alloy. All of the alloys studied, except the tin alloys, exhibited increasing precipitate (compound particles) with increasing alloy content. The precipitate tended to form along grain boundaries as illustrated in Figure 3 for zirconium-iron alloys. Thus it appeared that there might be a relationship between the compounds and hydriding susceptibility.

Zircaloy-2-Nickel Alloys

Experiments were conducted to determine the effect of nickel on hydrogen absorption in Zircaloy-2. Corrosion tests were conducted in degassed 680 F water with Zircaloy-2 containing 0.57, 0.03 (normal), and 0.002 weight percent nickel. The latter alloy was prepared at the Bettis Atomic Power Laboratory of the Westinghouse Electric Corporation as part of a program to study the effect on hydrogen absorption of eliminating nickel from Zircaloy-2.

Hydrogen absorption in these alloys as a function of total corrosion (weight

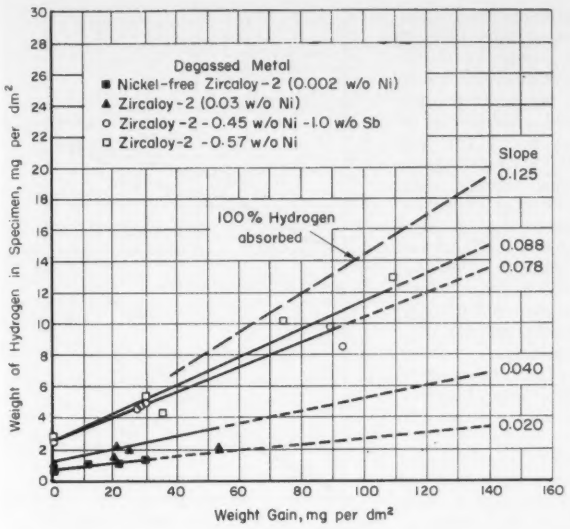


Figure 4—Hydrogen absorption in modified Zircaloy-2 exposed up to 107 days to static degassed or hydrogenated 680 F water.

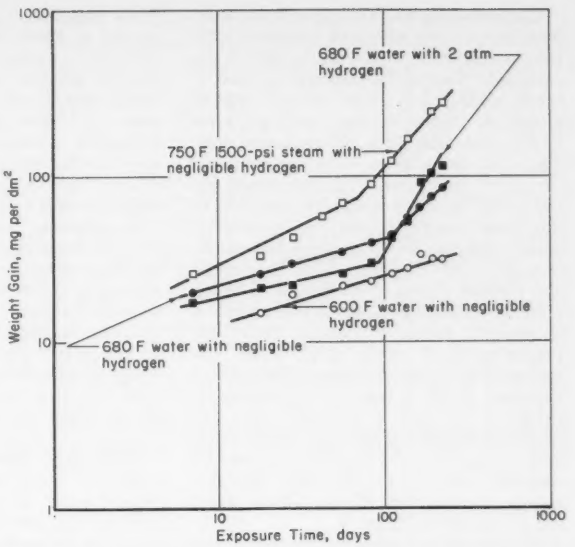

680 F water with 2 atm hydrogen
750 F 1500-psi steam with negligible hydrogen
600 F water with negligible hydrogen
680 F water with negligible hydrogen
Weight Gain, mg per dm²
Exposure Time, days

Figure 5—Corrosion rate curves for Zircaloy-2 containing 0.41 weight percent antimony addition.

TABLE 4—Summary of Corrosion and Hydrogen-Absorption Data for Zircaloy Exposed to 600 F Degassed Water

Alloy Base	Addition, Weight Percent	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²
Zircaloy-2 (1.60 Weight Percent Sn)	<0.001 Sb	56	24.7	1.48	224	34.2	2.05	...	....	....
	0.05 Sb	84	25.2	2.18	224	33.8	3.18	...	....	....
	0.20 Sb	28	23.2	1.75	224	39.3	3.24	...	....	....
	0.41 Sb	56	23.9	1.04	224	34.2	2.04	...	....	....
Modified Zircaloy-2 (1.05 Weight Percent Sn)	<0.001 Sb	28	23.6	1.58	168	40.2	2.50	...	....	....
	0.05 Sb	28	25.0	1.31	84	38.8	2.35	224	44.3	2.81
	0.14 Sb	28	24.5	2.13	56	39.6	3.00	224	50.8	3.80
	0.46 Sb	28	23.7	0.78	224	36.7	1.13	...	....	....
Modified Zircaloy-2 (0.31 Weight Percent Sn)	<0.001 Sb	28	25.5	0.68	56	44.1	1.31	112	60.0	1.73
	0.06 Sb	28	27.0	0.28	168	40.7	0.79	224	49.4	1.31
	0.17 Sb	...	....	....	28	43.0	0.83	112	60.6	1.14
	0.51 Sb	56	24.8	0.75	224	34.2	0.97	...	....	....
Zircaloy-2 (1.60 Weight Percent Sn)	0.03 As	28	26.1	0.75	168	41.6	1.91	...	....	....
	0.14 Te	28	28.6	1.48	56	40.4	2.17	224	47.5	2.09
	0.11 Bi	28	27.4	2.09	56	41.5	3.19	224	51.8	3.84

gain) for exposures ranging up to 107 days is shown in Figure 4. Also included in Figure 4 is a Zircaloy-2-0.45 weight percent nickel-1.0 weight percent antimony alloy which will be discussed later in the paper. A linear relationship was observed between hydrogen pickup and total weight gain. As anticipated, the slopes of these lines were not equal and increased with increasing nickel content. (Percentage of theoretical hydrogen absorbed for each alloy can be obtained by dividing the slope by 0.125 and multiplying by 100.) It is interesting to note that for the three alloys the hydrogen pickup doubled with a fifteenfold increase in nickel content.

Additives to Zircaloy

It is possible that the effect of nickel on hydrogen absorption in zirconium may be related to its low hydrogen overvoltage. It is known that during the electrolysis of aqueous solutions, very little polarization occurs on nickel cathodes. Hydrogen atoms associate into molecules which are then readily evolved from the cathode. Nickel also is capable of the reverse reaction of dissociating molecular hydrogen into atomic hydrogen. In this respect it is well known for its use as catalysts in hydrogenation reactions. It is conceivable that the nickel compounds in zirconium also may act as catalysts to promote hydrogen absorption. On the other hand, antimony, chromium, and iron compounds in zirconium probably have higher hydrogen overvoltages and do not possess catalytic activity.

Sulfur and other elements such as arsenic, antimony, bismuth, and tellurium are known to poison the catalytic effects of nickel in chemical reactions. A similar poisoning effect might be expected if nickel were acting as a cathode and a catalyst in promoting hydrogen pickup during the corrosion of Zircaloy-2.

Zircaloy-2-Nickel-Antimony Alloys

Based on the above line of reasoning, and the observed beneficial effects of antimony in sponge zirconium, alloys were prepared containing arsenic, antimony, bismuth, and tellurium additions to modified Zircaloy-2. The first such alloy consisted of 1.0 weight percent antimony addition to Zircaloy-2 containing 0.45 weight percent nickel. Corrosion data are presented in Figure 4 and indicate that hydrogen absorption in this alloy was about equal to that in a similar alloy containing no antimony. Thus the antimony addition did not influence hydrogen absorption in the Zircaloy-2-0.45 weight percent nickel alloy.

Zircaloy-Antimony, -Arsenic, -Bismuth, or -Tellurium Alloys

The effect of the above alloying additions in Zircaloy-2 of nominal nickel composition (0.05 weight percent) also was investigated. Antimony additions also were made to two modified Zircaloy-2 alloys containing, nominally, only 1.0 and 0.25 weight percent tin, respectively. Hydrogen absorption as a function of total corrosion was studied in exposures to high-temperature water and steam under (1) degassed conditions and (2) a small hydrogen overpressure.

Corrosion Rates. Test specimens were weighed periodically, and corrosion rates were established from the weight gains obtained. Specimens exposed to 600 F water and 750 F steam with 2 atmospheres of hydrogen were weighed after 7, 14, and 224 days of exposure only. Thus, corrosion rates were not obtained for these conditions. The corrosion behavior of the alloy specimens exposed to the other four conditions (600 and 680 F water and 750 F steam degassed condition plus 680 F water with hydrogen) was typical of that of Zircaloy-2. Log-log plots of weight gain versus time resulted in straight lines with initial slopes approaching 0.33. This same slope was maintained during the entire 224 days of exposure to 600 F water. The usual transition in kinetics to a linear rate was observed in 680 F water and 750 F steam under degassed conditions after exposures ranging from 65 to 135 days. Weight-change data typical of the alloys tested are presented in Figure 5.

Weight-change data for all the alloys in the six test conditions are given in Table 3. (These data were taken from log-log plots of the corrosion results and may not correspond exactly to values given in Tables 4 through 9.)

Direct comparisons can be made between the 2-atmospheres hydrogen and the degassed conditions in 680 F water. They indicate that transition in kinetics occurs at about the same time (100 to 120 days) under both conditions. However, in general, the pretransition rate of attack was lower and the posttransition rate was higher under 2 atmospheres of hydrogen. Comparisons at 14 and 224 days for the 600 and 750 F conditions revealed that higher weight gains were obtained with 2 atmospheres of hydrogen.

In general, antimony in the range of 0.05 to 0.5 weight percent had little or no effect on corrosion behavior. A notable exception occurred in 750 F steam, where increased corrosion was observed with increasing antimony contents at 224 days of exposure (after transition).

No improvement in corrosion resistance was observed with arsenic, bismuth, or tellurium additions to the Zircaloys.

Hydrogen Absorption. Postcorrosion hydrogen analyses were obtained at weight gains of approximately 25, 40, and 60 mg per dm² in an attempt to compare amounts absorbed (1) before, (2) at, and (3) after transition in reaction rates. The results are presented in Tables 4 through 9. Alloy specimens which were exposed to 600 F water and 750 F steam with 2 atmospheres of hydrogen were examined after 7, 14, and 224 days of exposure only. Thus, a number of analyses were not obtained at 40 mg per dm², and the analyses of posttransition specimens in 750 F steam were made at weight gains that were much higher than 60 to 70 mg per dm².

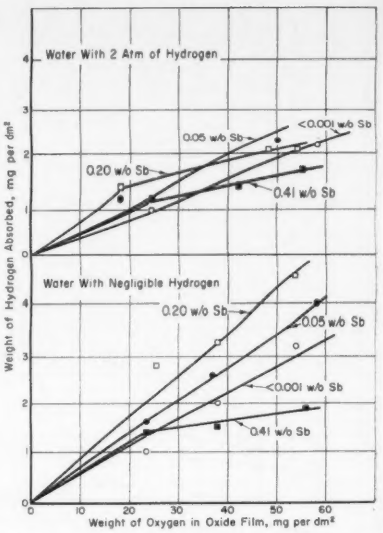


Figure 6—Hydrogen absorption as a function of total corrosion in 680 F water for Zircaloy-2 containing antimony additions.

In general, the amount of hydrogen absorbed varied linearly with the total

TABLE 5—Summary of Corrosion and Hydrogen-Absorption Data for Zircaloy Exposed to 680 F Degassed Water

Alloy Base	Addition, Weight Percent	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²
Zircaloy-2 (1.60 Weight Percent Sn)	<0.001 Sb	14	24.2	1.02	112	39.7	2.04	196	57.2	3.25
	0.05 Sb	14	25.0	1.57	56	39.8	2.62	140	61.7	4.03
	0.20 Sb	7	28.3	2.78	56	41.5	3.31	140	57.0	4.50
	0.41 Sb	14	24.9	1.35	84	39.8	1.48	140	57.9	1.89
Modified Zircaloy-2 (1.05 Weight Percent Sn)	<0.001 Sb	14	24.5	2.12	84	40.6	2.92	168	64.8	4.51
	0.05 Sb	..	....	....	7	39.0	2.36	112	58.9	5.09
	0.14 Sb	..	....	....	7	40.8	4.33	112	62.0	5.47
	0.46 Sb	7	25.3	1.08	56	40.0	1.47	140	68.3	1.98
Modified Zircaloy-2 (0.31 Weight Percent Sn)	<0.001 Sb	14	24.9	1.18	84	41.7	1.74	140	58.8	2.47
	0.06 Sb	28	24.9	0.57	84	38.7	1.23	196	60.1	2.68
	0.17 Sb	7	25.6	1.05	56	40.1	1.63	168	59.9	2.30
	0.51 Sb	14	23.7	1.04	84	41.7	1.46	196	59.3	2.49
Zircaloy-2 (1.60 Weight Percent Sn)	0.03 As	7	24.4	0.80	56	42.7	2.32	140	55.7	3.30
	0.14 Te	..	....	....	7	41.2	3.06	140	65.4	2.12
	0.11 Bi	..	....	....	7	40.3	2.13	112	59.9	6.29

TABLE 6—Summary of Corrosion and Hydrogen-Absorption Data for Zircaloy Exposed to 750 F 1500-PSI Degassed Steam

Alloy Base	Addition, Weight Percent	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²
Zircaloy-2 (1.60 Weight Percent Sn)	<0.001 Sb	14	26.0	1.55	42	38.8	1.74	140	69.9	2.61
	0.05 Sb	7	26.2	1.54	28	40.3	2.27	112	71.6	3.69
	0.20 Sb	7	24.7	1.30	28	37.7	2.34	112	72.7	3.82
	0.41 Sb	7	25.9	1.07	28	41.2	1.87	...	....	....
Modified Zircaloy-2 (1.05 Weight Percent Sn)	<0.001 Sb	7	25.7	1.93	42	39.4	3.09	168	70.1	4.34
	0.05 Sb	28	27.3	2.74	42	40.2	3.13	140	71.8	4.38
	0.14 Sb	7	24.6	2.17	42	42.0	3.64	196	86.8	5.81
	0.46 Sb	7	24.4	1.54	42	40.7	2.84	112	71.8	4.14
Modified Zircaloy-2 (0.31 Weight Percent Sn)	<0.001 Sb	7	24.8	1.43	42	39.7	1.76	196	70.4	3.31
	0.06 Sb	28	28.3	1.17	42	40.3	1.58	168	67.4	2.46
	0.17 Sb	7	24.0	1.38	28	39.4	2.01	168	66.8	3.01
	0.51 Sb	7	25.0	1.48	42	40.8	2.14	112	69.5	2.36
Zircaloy-2 (1.60 Weight Percent Sn)	0.03 As	7	25.1	0.95	28	39.1	1.64	112	79.3	3.68
	0.14 Te	7	25.1	1.30	28	43.0	2.14	112	72.8	3.58
	0.11 Bi	7	25.6	1.90	28	40.5	2.56	112	73.0	4.77

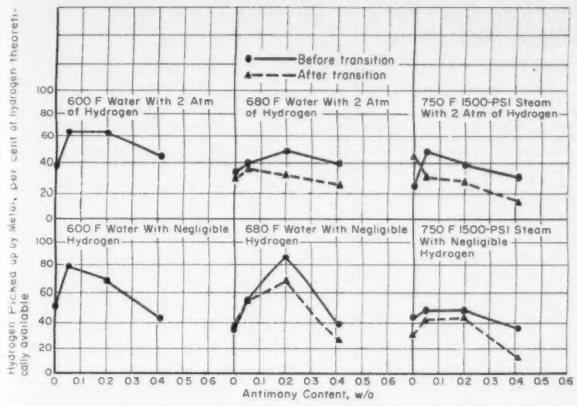

Before transition
After transition
600 F Water With 2 Atm of Hydrogen
680 F Water With 2 Atm of Hydrogen
750 F 1500-PSI Steam With 2 Atm of Hydrogen
600 F Water With Negligible Hydrogen
680 F Water With Negligible Hydrogen
750 F 1500-PSI Steam With Negligible Hydrogen
Hydrogen Picked up by Metal, per cent of hydrogen theoretically available
Antimony Content, w/o

Figure 7—Percentage of theoretically available hydrogen from corrosion that is absorbed in the metal as a function of antimony content in Zircaloy-2.

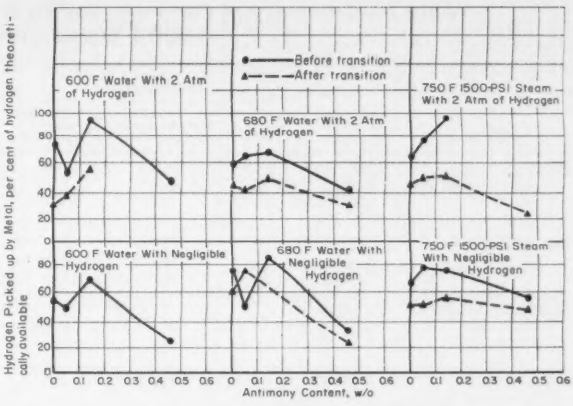

Before transition
After transition
600 F Water With 2 Atm of Hydrogen
680 F Water With 2 Atm of Hydrogen
750 F 1500-PSI Steam With 2 Atm of Hydrogen
600 F Water With Negligible Hydrogen
680 F Water With Negligible Hydrogen
750 F 1500-PSI Steam With Negligible Hydrogen
Hydrogen Picked up by Metal, per cent of hydrogen theoretically available
Antimony Content, w/o

Figure 8—Percentage of theoretically available hydrogen from corrosion that is absorbed in the metal as a function of antimony content in modified Zircaloy-2 (1.05 weight percent tin).

amount of corrosion. However, a sufficient number of plots resulted in curves to cast some doubt on the linear relationship. Examples of both types are shown in Figure 6.

The ratio of hydrogen absorbed to that produced from corrosion of a given sample is expressed as a percentage of theoretical and plotted as a function of antimony content in Figures 7, 8, and 9. The curves for posttransition hydrogen absorption generally were lower than those for pretransition. This again suggests a nonlinear relationship between hydrogen absorption and total corrosion. However, the curves generally were parallel and indicated that antimony additions in Zircaloy do not result in a marked reduction in hydrogen absorption. In fact, in the range of 0.1 to 0.2 weight percent antimony, the percentage of theoretical absorption usually was higher than that of the base alloy or the 0.5 weight percent antimony alloy.

It is interesting to note from Figures 7, 8, and 9 that the modified Zircaloy-2 alloys containing 0.31 weight percent tin exhibited the lowest percentages of theoretical absorption. These alloys differed from the other Zircaloys not only in that they were low in tin (0.31 weight percent) but also were high in iron (0.24 weight percent).

No reduction in percentage of theoretical hydrogen absorption was obtained with additions of arsenic, bismuth, or tellurium to the Zircaloys.

Discussion and Conclusions

The results of these experiments have further demonstrated that relatively small quantities of nickel (at about 0.05 weight percent) in zirconium or Zircaloy-2 result in increased hydrogen absorption during corrosion in high-temperature water and steam. It has also been shown that, of the other elements common to Zircaloy-2, tin has little or no effect on hydrogen absorption, while iron and chromium decrease hydrogen absorption in sponge-base binary alloys. Minimum absorption was observed in the vicinity of 0.1 to 0.2 weight percent additions in the latter alloys.

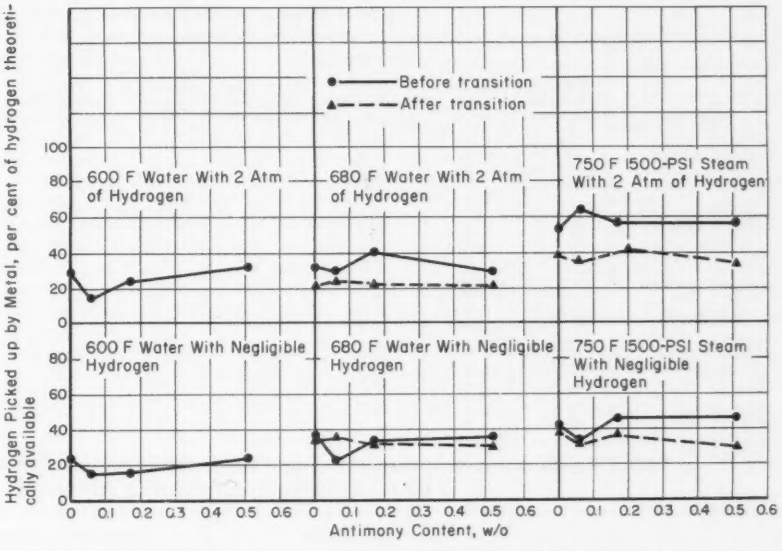

Before transition
After transition
600 F Water With 2 Atm of Hydrogen
680 F Water With 2 Atm of Hydrogen
750 F 1500-PSI Steam With 2 Atm of Hydrogen
600 F Water With Negligible Hydrogen
680 F Water With Negligible Hydrogen
750 F 1500-PSI Steam With Negligible Hydrogen
Hydrogen Picked up by Metal, per cent of hydrogen theoretically available
Antimony Content, w/o

Figure 9—Percentage of theoretically available hydrogen from corrosion that is absorbed in the metal as a function of antimony content in modified Zircaloy-2 (0.31 weight percent tin).

Although the addition of antimony to sponge zirconium results in a marked decrease in hydrogen absorption during corrosion of binary alloys, it produces little or no effect when added to Zircaloy-2. Additions of arsenic, bismuth, or tellurium to Zircaloy-2 also do not affect hydrogen absorption during corrosion.

A 2-atmosphere partial pressure of hydrogen over the 600 and 680 F water or 750 F steam did not result in increased hydriding of Zircaloy-2 above that observed under degassed conditions.

Based on present information, it is suggested that corrosion and hydrogen absorption in zirconium alloys during exposure to high temperature water or steam can be described by the following paragraphs.

The oxide which forms on crystal-bar zirconium (thermal decomposition of zirconium iodide) may be protective during initial exposures to high-temperature water. However, the film eventually reaches a certain thickness at which the internal stresses in the film cause it to rupture and it no longer is protective. The time to loss of protection decreases as the temperature increases—it may be only a matter of hours at 750 F. At these high temperatures the oxide film is not completely protective even during initial exposure and affords access to the underlying metal. Thus a portion of the hydrogen from the corrosion reaction is able to react with the zirconium.

The addition of tin to zirconium does not improve the quality of the oxide film and hence would not be expected to affect hydrogen absorption appreciably.

Chromium, iron, and nickel have extremely limited solubility in zirconium, and precipitates (apparently compounds of these elements) are formed at levels as low as several hundred ppm. If these precipitates are present as discrete particles, a marked improvement in corrosion resistance results. It is suggested that these compound particles are strongly cathodic to the zirconium matrix and the resulting potential difference is sufficient to anodically polarize the zirconium. This

TABLE 7—Summary of Corrosion and Hydrogen-Absorption Data for Zircaloy Exposed to 600 F Water with 2 ATM of Hydrogen

Alloy Base	Addition, Weight Percent	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²
Zircaloy-2 (1.60 Weight Percent Sn)	<0.001 Sb	224	33.3	1.32	224	40.2	2.09	...	....	....
	0.05 Sb	14	25.2	1.81	224	44.2	3.44	...	....	....
	0.20 Sb	..	....	....	224	39.9	3.12	224	53.3	3.63
	0.41 Sb	..	....	....	224	47.8	2.59	224	51.2	2.69
Modified Zircaloy-2 (1.05 Weight Percent Sn)	<0.001 Sb	14	26.5	2.37	224	49.8	3.88	224	59.4	3.88
	0.05 Sb	14	26.3	1.61	224	41.0	2.56	224	55.0	2.56
	0.14 Sb	14	23.3	2.46	...	....	....	224	53.6	3.52
	0.46 Sb	14	24.9	1.11	224	39.8	2.72	...	....	....
Modified Zircaloy-2 (0.31 Weight Percent Sn)	<0.001 Sb	..	....	....	14	41.5	1.36	224	65.5	2.10
	0.06 Sb	14	26.4	0.33	...	....	....	224	60.2	1.37
	0.17 Sb	..	....	....	224	35.2	0.82	224	71.4	2.39
	0.51 Sb	..	....	....	224	40.3	1.52	...	....	....
Zircaloy-2 (1.60 Weight Percent Sn)	0.03 As	14	26.5	0.89	224	41.9	1.19	...	....	....
	0.14 Te	..	....	....	14	38.4	2.33	224	55.2	1.99
	0.11 Bi	..	....	....	14	39.5	3.12	224	63.1	4.43

TABLE 8—Summary of Corrosion and Hydrogen-Absorption Data for Zircaloy Exposed to 680 F Water with 2 ATM of Hydrogen

Alloy Base	Addition, Weight Percent	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²
Zircaloy-2 (1.60 Weight Percent Sn)	<0.001 Sb	56	25.1	1.02	...	....	....	168	60.3	2.17
	0.05 Sb	56	24.4	1.18	...	....	....	168	52.3	2.32
	0.20 Sb	56	24.7	1.44	140	50.4	2.08	140	56.0	2.08
	0.41 Sb	56	25.6	1.24	140	42.9	1.44	140	57.0	1.73
Modified Zircaloy-2 (1.05 Weight Percent Sn)	<0.001 Sb	56	25.1	1.71	168	37.4	2.26	168	58.4	2.71
	0.05 Sb	56	25.1	1.90	168	46.6	2.52	168	57.8	2.85
	0.14 Sb	56	26.1	2.05	140	38.9	2.61	168	59.7	2.98
	0.46 Sb	56	24.9	1.26	140	45.7	1.87	168	55.6	1.87
Modified Zircaloy-2 (0.31 Weight Percent Sn)	<0.001 Sb	56	24.4	0.97	168	34.2	1.15	168	62.6	1.38
	0.06 Sb	56	25.1	0.91	168	37.9	1.27	168	66.7	1.76
	0.17 Sb	56	25.0	1.13	168	36.2	1.76	168	68.4	1.83
	0.51 Sb	56	25.0	0.93	...	....	....	168	68.0	1.86
Zircaloy-2 (1.60 Weight Percent Sn)	0.03 As	56	25.5	1.40	140	50.3	1.86	168	58.3	2.03
	0.14 Te	56	24.6	0.80	140	45.0	1.14	168	69.6	1.70
	0.11 Bi	56	24.9	1.71	140	40.1	2.40	168	68.1	3.50

TABLE 9—Summary of Corrosion and Hydrogen-Absorption Data for Zircaloy Exposed to 750 F 1500-PSI Steam with 2 ATM of Hydrogen

Alloy Base	Addition, Weight Percent	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²	Exposure Time, Days	Total Weight Gain, mg per dm²	Hydrogen Absorbed, mg per dm²
Zircaloy-2 (1.60 Weight Percent Sn)	<0.001 Sb	7	25.3	0.85	...	....	....	224	41.5	4.86
	0.05 Sb	7	26.7	1.54	...	....	....	224	158.0	5.92
	0.20 Sb	7	25.7	1.19	...	....	....	224	166.0	5.75
	0.41 Sb	..	....	....	7	41.1	1.56	224	278.0	5.01
Modified Zircaloy-2 (1.05 Weight Percent Sn)	<0.001 Sb	7	27.3	2.03	...	....	....	224	98.0	5.34
	0.05 Sb	7	26.3	2.32	...	....	....	224	110.0	5.87
	0.14 Sb	7	26.1	2.81	14	39.7	2.71	224	122.0	6.66
	0.46 Sb	..	....	....	...	....	....	224	161.0	4.67
Modified Zircaloy-2 (0.31 Weight Percent Sn)	<0.001 Sb	7	24.9	1.58	...	....	....	224	83.2	3.85
	0.06 Sb	14	24.8	1.85	...	....	....	224	85.9	3.66
	0.17 Sb	7	25.8	1.73	...	....	...	224	92.2	4.60
	0.51 Sb	7	26.1	1.74	...	....	....	224	144.0	4.67
Zircaloy-2 (1.60 Weight Percent Sn)	0.03 As	7	28.0	1.32	...	....	....	224	156.0	6.88
	0.14 Te	..	....	....	...	....	....	...	....	....
	0.11 Bi	7	25.9	1.73	...	....	....	224	147.0	7.09

results in the formation of a thin protective oxide film over the zirconium.

A similar theory has been proposed for the behavior of iron and nickel compounds in aluminum[8] and for palladium compounds in zirconium.[9] This explanation also could account for the corrosion resistance of sponge zirconium which contains in the neighborhood of 500 ppm iron as an impurity.

It is also believed that the chromium, iron, and nickel compounds possess a low hydrogen overvoltage. The hydrogen ions from the corrosion reaction form on the surface of the oxide and migrate to the vicinity of the cathodic compounds. They are discharged by electrons migrating outward through the oxide film. In the case of iron and chromium alloys the hydrogen atoms are readily associated into molecules and pass into the water rather than diffusing through the oxide film. However, a small percentage do migrate through the oxide film and react with the underlying metal. This diffusion probably occurs in the vicinity of the compound particles. The oxide film has been observed to grow faster over the compound particles.[10,11] Thus diffusion apparently occurs more readily at these areas.

The nickel compounds, on the other hand, apparently do not associate the corrosion hydrogen. Thus, concentrations of hydrogen atoms (or ions) build up in the vicinity of the nickel compounds. The hydrogen diffuses through the more porous oxide over the particles and then reacts with the underlying metal. The passage of hydrogen through the oxide film apparently has no disrupting effect. The present work has shown that the binary nickel alloys were more corrosion resistant than Zircaloy-2. The absence of any beneficial effects of antimony, arsenic, bismuth, or tellurium additions in reducing hydrogen absorption in Zircaloy-2 does not necessarily refute the proposed catalytic effect of nickel. Instead it may indicate that the addition of these elements is not an effective method to "poison" the nickel compounds.

The improved corrosion resistance and decreased hydrogen absorption obtained with antimony additions to sponge zirconium may be explained in several ways. Published information indicates complete solubility of antimony in zirconium at the levels studied in this program.[12] The zirconium oxide formed during corrosion in high-temperature water is an anion-deficit semiconductor in which oxygen migration via anion vacancies is the rate-controlling step in corrosion. The incorporation of cations of higher valence than Zr^{+4}, such as Sb^{+5}, into the oxide lattice should reduce the number of vacancies. Providing the mobility of the vacancies was not increased, the oxygen diffusion in the film would decrease and corrosion resistance would improve. The more resistant film also could be more resistant to hydrogen diffusion. On the other hand, the present study has indicated increasing precipitate (compounds) with increasing antimony content. The compounds may have contained antimony and iron, with the iron coming from the sponge melting stock. In this event, the compound particles could have been cathodic and the same mechanism would apply as described for the iron compounds.

The transport of hydrogen throughout the microstructure of the corrosion-tested alloys apparently occurs by diffusion. At the corrosion-test temperatures the solubility of hydrogen in zirconium is several hundred ppm. Thus, if hydrides were formed at the metal-oxide interface, the hydrogen would subsequently dissolve in the zirconium, and then diffuse inward under the driving force of the concentration gradient. The absence of a surface hydride layer in the zirconium indicates that the diffusion rate is more rapid than the rate of formation of the hydride. When the corrosion specimens are cooled to room temperature the solubility limit for hydrogen (about 20 ppm) is exceeded, and zirconium hydride needles are precipitated.

Hydrogen concentrations of upwards of 500 ppm were found in nickel-zirconium alloys. The hydride needles appeared to be uniformly distributed throughout the specimens when examined at room temperatures. For uniform distribution of this concentration to occur as described above it would be necessary for the nickel-zirconium compound itself to have a high solubility for hydrogen or to increase the solubility for hydrogen in zirconium at the corrosion-test temperatures. It is known that at least one of the nickel-zirconium compounds (ZrNi) can be hydrided to a greater extent than zirconium.[13]

An alternate explanation would be the diffusion of hydrogen through zirconium hydride. A high partial pressure of hydrogen is necessary for this to occur.[14]

Many of the points raised in this discussion are based on conjecture. To further clarify the concepts it would be desirable to prepare alloys having the composition of the iron, chromium, and nickel compounds. (The zirconium-rich compounds $ZrFe_3$, $ZrCr_2$, and Zr_2Ni, are those most likely to be present at low alloying levels.) The properties of these compound alloys should be compared at corrosion-test temperatures with those of unalloyed zirconium on the basis of: (1) corrosion behavior, (2) electrode potentials, (3) hydrogen diffusion rates, and (4) terminal solubility of hydrogen.

Acknowledgments

Work described in this paper was performed under AEC Contract No. W-7405-eng-92. The authors wish to express their appreciation to the Battelle staff members who contributed to this study, including J. S. DiPesa and B. E. White who melted and fabricated the alloys, M. A. VanCamp, who performed the hydrogen assays, and W. N. Stiegelmeyer, who conducted the metallographic examinations.

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Any discussion of this article not published above will appear in June, 1961 issue.

Anodic Polarization of Lead-Platinum Bielectrodes In Chloride Solutions*

By L. L. SHREIR

Abstract

An account is given of potential-time studies made to determine the effect of a platinum microelectrode on the behavior of lead in chloride solutions. Topics discussed include current through platinum electrode, effect of relative areas of platinum/lead on potential, effect of withdrawal and insertion of platinum, weight change during anodic polarization, formation of lead peroxide films and use for cathodic protection of platinum-lead bielectrodes. It is considered that the platinum microelectrode serves to: (1) limit the initial formation of lead chloride, (2) oxidize plumbous ions to lead peroxide, (3) act as a "chlorine valve" so that lead chloride formation is prevented during operation. 3.8.3, 6.3.8

Introduction

ALTHOUGH PLATINUM is widely used as an inert anode in various electrolytic processes, the high cost of the metal limits its application. Recently, there has been considerable interest in more economical anodes consisting of a thin coating of platinum (0.00005 inch) applied to metals such as tantalum, titanium and zirconium.

Cotton[1] has observed that although titanium pits and rapidly corrodes when anodically polarized at high current densities in chloride solutions, it remains passive when a comparatively small electrode of platinum is welded to the metal surface. Cotton has shown also that a similar effect could not be obtained with copper, aluminum or stainless steel, indicating that the oxide film on titanium is resistant to penetration by chloride ions.

It is apparent that when a titanium-platinum bielectrode is anodically polarized in chloride solutions, film growth on the titanium proceeds to a limiting thickness only; the high resistance of the film then causes electron current to flow through the platinum and film growth ceases. The system may be regarded either as (1) a platinum anode supported by a metallic conductor which is insulated by its own oxide, or (2) as a $Ti\text{-}TiO_2$ system in which the presence of platinum prevents the potential across the oxide increasing to a value where film breakdown and pitting occurs. With titanium in chloride electrolytes this potential is ~12-14 V, whereas very high potentials can be applied to tantalum without producing pitting.[2] These metals are characterized by forming dielectric oxide films during anodic polarization so that the entire current passes through the platinum.

There is, however, a further possibility. Lead peroxide has an electrical conductivity[3] of 0.94-4.05 x 10^{-4} ohm. cm. which is comparable to that of a metal. $Pb\text{-}PbO_2$ anodes have several applications. The use of a 1 percent Ag/Pb alloy for electrowinning is well known and was first suggested as an anode for cathodic protection by H. Wheeler[4] following laboratory trials. A 2 percent Ag/Pb alloy has been investigated recently for use in the Canadian Navy[5] and a 1 percent Ag/6 percent Sb/lead alloy is in commercial use.[6] Crennell[4] considers that the 1 percent Ag addition to lead provides an anode which is satisfactory up to 10 Amp/ft² but at higher current densities—say over 15 Amp/ft², a film of high electrical resistance may be produced. There appears to be no satisfactory explanation of the role of silver in promoting formation of lead peroxide.

During a study of the anodic polarization of lead and lead alloys in seawater it was considered that the introduction of a platinum microelectrode into the lead surface might produce a fundamental change in the electrode process and result in the formation of lead peroxide rather than plumbous chloride. Some details have been reported previously by Shreir and Weinraub.[7,8]

The present work describes some preliminary results of potential-time studies which serve to illustrate the effect of a platinum microelectrode on the behavior of lead in chloride solutions.

Experimental

Lead Anodes

The lead used was "commercial high purity" (supplied by Associated Lead Ltd., England) having an analysis of >99.9 percent lead and was used in the form of an anode 1 inch x 1 inch diameter (Figure 1). Connection to the conducting wire was made using an unplasticized polyvinyl chloride holder and neoprene washer to prevent ingress of the electrolyte. The end of the anode was rounded and the total area of the anode exposed to the electrolyte was 3.5 in.² For certain experiments a 1 percent Ag/Pb alloy was used.

Platinum wire, ½ inch long, was introduced into the lead by drilling a hole slightly larger than the diameter of the wire, inserting the wire so that ⅛ inch projected and peening the lead surrounding the platinum. This simple procedure ensured that the platinum was firmly secured to the lead surface and gave a satisfactory electrical connection. For convenience, the different positions of the platinum microelectrodes used will be referred to by the letters "a" and "b" shown in Figure 1.

Prior to electrolysis, the surface of the lead was cleaned by scraping with a razor blade.

Cathode

A sheet steel cathode, 6 inch x 4 inch, was used in all experiments and was placed 6 inches from the lead anode.

Electrolyte

Electrolysis was carried out in a glass cell containing 4 liters of 0.5M NaCl. Fresh electrolyte was used for each experiment to ensure that hypochlorite formed during electrolysis was kept to a minimum. Certain tests, of a more prolonged nature, were carried out in artificial sea-water[9] using 5 gallons of solution.

Potential-Time Curves

Direct current was provided by rectified a-c from a rectifier-transformer as used for cathodic protection installations. The output voltage had 1 percent a-c. Current control was effected by means of

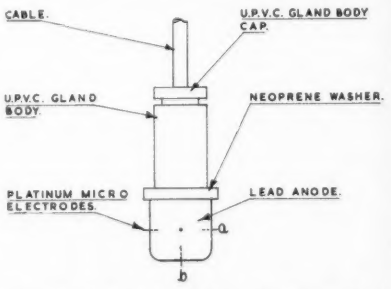

Figure 1—Method of mounting a lead anode. Platinum microelectrodes are at positions "a" and "b" (four microelectrodes could be inserted in positions "a".)

About the Author

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★ Submitted for publication May 10, 1960.

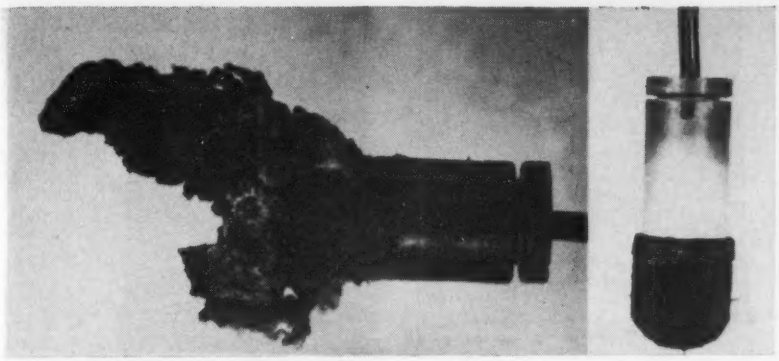

Figure 2—Anodic polarization of lead in artificial sea water. Left: pure lead, 30 Amp/ft² for 16 hours; right: 1 percent Ag/Pb with platinum microelectrodes after 200 hours at 200 Amp/ft².

a variable transformer and rheostats. The potential of the lead-electrolyte interface was determined by a Luggin capillary and calomel half-cell (saturated KCl, E = 0.2422 V.) in conjunction with a valve voltmeter. All potentials given are relative to this electrode. To avoid interfering with film formation the capillary was arranged so that it was very close but not actually touching the lead surface. The small IR drop through the electrolyte was considered negligible for the purpose of the present work.

Results

Effect of Platinum Microelectrode on Lead

The behavior of lead when anodically polarized in 0.5 M KCl electrolyte was not reproducible and appeared to depend on the mode of crystallization of the lead chloride. At current densities up to 30 Amp/ft² the lead chloride did not appear to form a coherent deposit on the lead surface and continued passage of current resulted in complete disintegration of the anode (see left side of Figure 2). Appreciable amounts of lead peroxide were produced in the electrolyte and on the surface of the lead chloride coating the anode. A typical potential-time curve at 30 Amp/ft² (Figure 3) shows that the potential rises rapidly to a maximum of 18 V and then fluctuates from 14 to 18 V during subsequent passage of current. In certain experiments, however, particularly at higher current densities, the lead chloride was observed to form a thick, compact, coherent deposit. In such cases voltages as high as 70-90 V were required to maintain the current (50 Amp/ft²). Figure 2 (right side) shows a 1 percent Ag-Pb anode, containing platinum micro-electrodes, after 200 hours at 200 Amp/ft².

Figure 4 shows the results obtained using lead anodes containing two microelectrodes of platinum (0.020 inch diameter, position "a") polarized at 30 Amp/ft² (curve B) and 60 Amp/ft² (curve A).

The curves are characterized by an initial rapid increase in potential, similar to that observed with lead alone, and after reaching a peak potential (4.8 V at 30 Amp/ft², 7.2 V at 60 Amp/ft²) the potential gradually falls to a value of ~2 V. Observation of the platinum during the experiment showed that evolution of gas appeared to coincide with the peak potential. The anodes were found, on removal from the electrolyte, to be coated with a soft spongy deposit of lead peroxide although even after 4 hours small areas of lead chloride were visible. More prolonged electrolysis (24 hours) appeared to cause consolidation of the lead peroxide which then formed a continuous, hard, coherent coating on the lead surface. After this period there was no evidence of lead chloride on the surface. Under carefully controlled conditions it was possible to obtain, in certain cases, an anode which revealed that initially the lead peroxide formed around the platinum microelectrodes and then subsequently extended over the lead surface (Figure 5). This effect, however, was not reproducible; usually the lead peroxide appeared to form on all parts of the lead surface and appreciable amounts passed into the electrolyte. It is of interest to observe that very little lead peroxide deposited on the platinum which projected into the electrolyte.

Effect of Relative Areas of Platinum/Lead

As the size and number of the platinum microelectrodes are clearly of practical importance it was considered of interest to examine anodes containing a variety of platinum microelectrodes. Details of the bielectrodes are given in Table 1 and the results of potential-time studies in Figures 6 and 7. The specimens used to obtain the results given in Figure 7 consisted of lead rod (0.39 inch x 0.39 inch section) mounted in an epoxy resin so that 0.15 in² was exposed to the electrolyte and the platinum wire was inserted in the center.

All curves are again characterized by a rapid increase in potential followed by a gradual decrease to a steady state potential of 1.5 V to 2.0 V (Figure 7). Curve A is of particular interest showing that a platinum wire as small as 0.003 inch diameter, inserted in lead of area 3.5 in.², is capable of fundamentally changing the electrode processes. Similar results have been obtained by embedding particles of iridium powder in the lead surface or by using a graphite microelectrode.

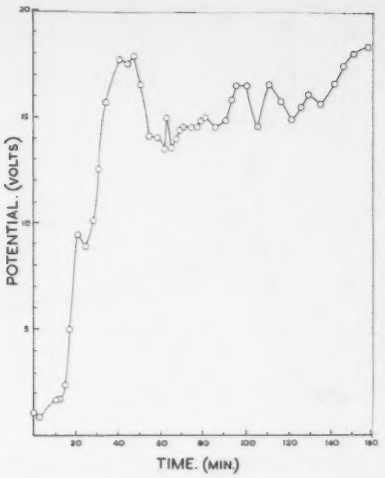

Figure 3—Potential-time curve for lead anodically polarized at 30 Amp/ft² in 0.5 M NaCl (potentials relative to saturated calomel).

In general, it would appear that for bielectrodes of similar geometry, the larger the ratio of lead to platinum the higher the maximum potential and the more prolonged is the time required for attainment of a steady state potential. However, even the smallest microelectrode appears to be capable of stabilizing a coating of lead peroxide on the metal surface.

Effect of Withdrawal and Insertion of Platinum

Figure 8 shows the effect of removing the platinum microelectrodes (2 wires, 0.020 inch diameter at position "a") from a bielectrode which had been anodically polarized at 30 Amp/ft² for 24 hours. The steady state potential was 1.5 V and the lead was observed to be uniformly coated with lead peroxide. Removal of the platinum (R) resulted in a rapid increase in potential and the simultaneous formation of lead chloride which could be observed in the electrolyte as streamers diffusing away from the anode.

Figure 9 was obtained by first anodically polarizing lead (without platinum) at 30 Amp/ft² for two hours, the potential reaching approximately 18 V. The anode was then removed from the electrolyte, a platinum microelectrode inserted (0.050 inch diameter position "a") and the bielectrode returned to the electrolyte and electrolysis continued. Two characteristic curves, A and B are shown in Figure 9. Curve A is characterized by a hump whereas Curve B shows a continuous decrease in potential to ~ 3.0 V after 60 minutes; more prolonged electrolysis resulted in a further decrease to ~ 1.7 V.

Effect of Platinum Microelectrode on Lead Peroxide Formed in Sulfuric Acid

A thin lead peroxide film was produced by anodizing in sulfuric acid and a platinum microelectrode was then inserted in the lead. On polarizing in sodium chloride solution the potential-time curve was observed to be similar to that shown in Figure 4 (Curve A). These results, and

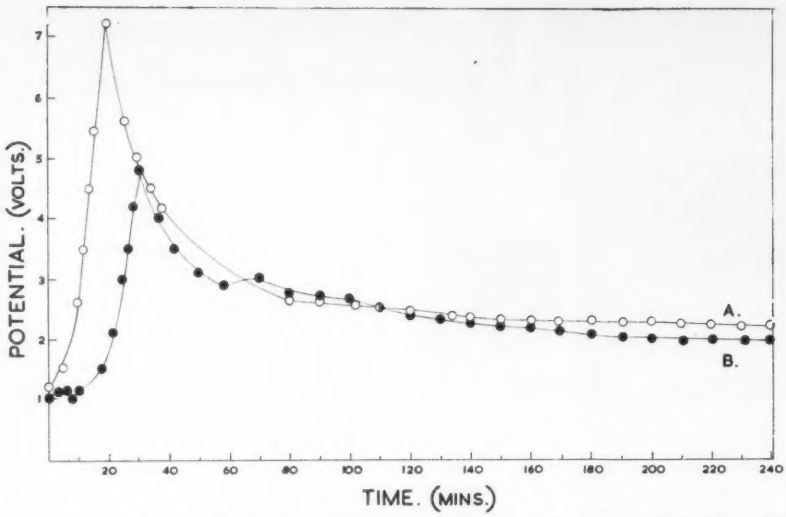

Figure 4—Effect of current density. Lead-platinum (microelectrodes, 2a) in 0.5 M NaCl at 30 Amp/ft² (curve A) and 60 Amp/ft² (curve B).

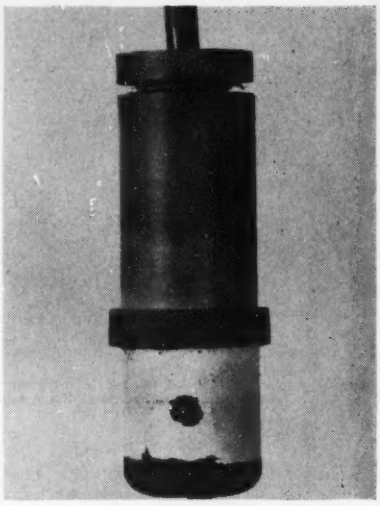

Figure 5—Formation of lead peroxide around the platinum microelectrodes.

observations of the anode, showed that the preformed lead peroxide had very little effect on the process and it would appear that lead chloride formation was a necessary prerequisite for subsequent formation of lead peroxide.

Current Through Platinum Microelectrode

Although with titanium-platinum bielectrodes all the current passes through the platinum, observations of the platinum of a lead-platinum bielectrode indicated that the evolution of chlorine appeared to be small and only varied slightly with increasing current.

Curve A of Figure 10 is a potential-current density curve for a platinum electrode in 0.5M sodium chloride. Curves B and C are corresponding curves for a platinum microelectrode and lead peroxide respectively of a lead-platinum bielectrode. From the potential and area of the microelectrode it is possible to obtain from Curve A the current density and current. The results are given in Table 2 which shows that the current density on the platinum is less than that on the lead peroxide, and that this effect becomes more pronounced with increasing current density. This presumably is due to the fact that, although the true area of the platinum approximates to its apparent value, there is a large discrepancy between these values for the lead peroxide owing to the very large roughness factor.

Weight Change During Anodic Polarization

Figure 11 shows the change in weight of a pure lead, 6 percent Sb/Pb and 1 percent Ag/Pb, containing two 0.020 inch diameter platinum microelectrodes (position "a"), during polarization in artificial sea water at 30 Amp/ft². The weight of the anode was approximately 180 gm. The 6 percent Sb/Pb alloy gave the most pronounced weight increase and sections of the lead showed that the lead peroxide formed a comparatively thick film.

TABLE 1—Variation of Ratio of Area of Lead/Platinum

Figure	Area of Lead, Inches²	Dia. of Platinum, (Inches)	No. and Position of Platinum Electrodes	Area of Lead/Area of Platinum	Maximum Voltage, V
6A	3.5	0.003	1 (a)	3000	5.7
6B	3.5	0.020	2 (a)	233	4.8
6C	3.5	0.050	5 (4a, 1b)	35	4.1
7A	0.15	0.003	1, Center	125	4.8
7B	0.15	0.020	1, Center	19	3.4
7C	0.15	0.050	1, Center	7.7	3.1

Discussion

It is apparent from the present study that a microelectrode of a noble metal inserted in a lead surface can result in the formation of a stable coating of lead peroxide on lead during anodic polarization in chloride solutions. This effect, which can be caused by a platinum wire of only 0.003 inch diameter or a few crystals of iridium, provides a bielectrode which can be used at high current densities in chloride solutions without the formation of a high resistance film of lead chloride.

Although further studies are necessary to establish the exact mechanism of the process, certain conclusions are possible from the present study.

It is considered that the following reactions are relevant:

$$Pb^{++} + 2e = Pb,$$
$$E = -0.126 + 0.030 \log a_{Pb^{++}} \quad (1)$$

$$PbO_2 + 4H^+ + 2e = Pb^{++} + 2H_2O,$$
$$E = 1.482 - 0.118\ pH - 0.030 \log a_{Pb^{++}} \quad (2)$$

$$Cl_2 + 2e = 2Cl^-,$$
$$E = 1.36 + 0.059 \log p_{Cl_2} - 0.030 \log a_{Cl^-} \quad (3)$$

$$PbCl_2 = Pb^{++} + 2Cl^-,$$
$$K = 1.6 \times 10^{-5} \quad (4)$$

The assumption that lead peroxide is formed by oxidation of plumbous ions appears justified owing to the solubility of lead chloride and to the fact that oxidation of lead sulfate to peroxide occurs through the solution.[10] It is possible, however, that during prolonged anodizing, film growth of the lead peroxide may result from direct oxidation of the metal. Considering first lead alone, it is appar-

TABLE 2—Current Passing Through Platinum

Lead-platinum bielectrode, three platinum microelectrodes, 0.020" dia. at positions a, a, b. 0.5M sodium chloride.

Current Density, Amp/ft²	Total Currents, Amps	Current Density on Platinum, (Amp/ft²)	Current Through Platinum, Amps
10	0.24	5.8	0.00061
20	0.48	6.2	0.00068
30	0.73	7.0	0.00077
40	0.97	7.5	0.0008
50	1.21	8.0	0.00085
60	1.46	8.5	0.00092
70	1.70	9.0	0.00095
80	1.94	10.0	0.0010
90	2.18	10.5	0.0011
100	2.43	11.0	0.00117
120	3.92	11.5	0.00123
150	3.64	12.0	0.00127
180	4.36	13.0	0.00138
200	4.86	13.8	0.00148

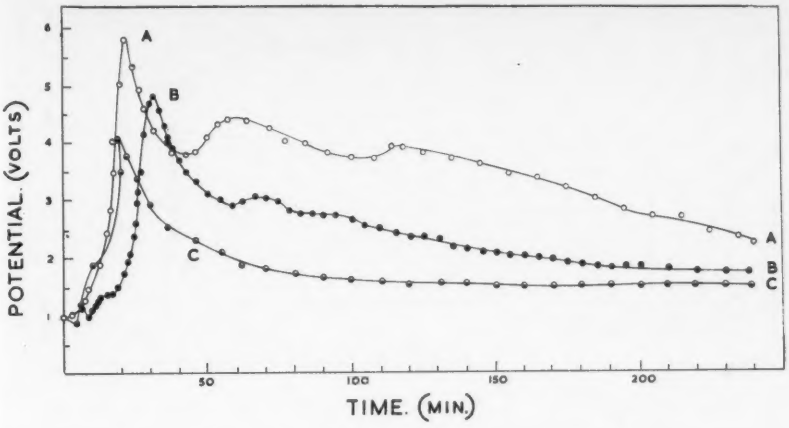

Figure 6—Effect of relative areas of lead to platinum for 30 Amp/ft² in 0.5 M NaCl.

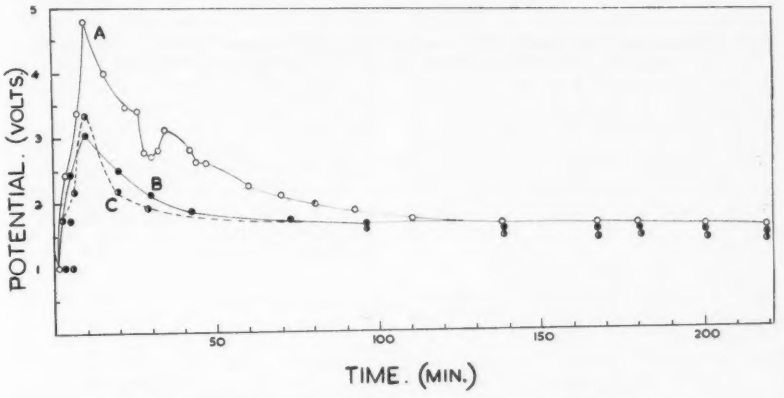

Figure 7—Effect of relative areas of lead to platinum for 30 Amp/ft² in 0.5 M NaCl.

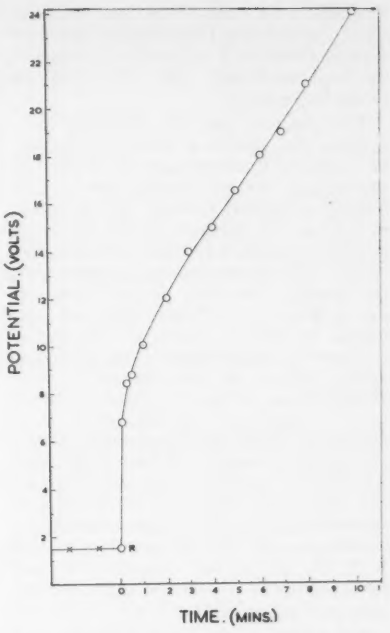

Figure 8—Withdrawal of platinum microelectrodes at position "a" (2) after prior polarization in 0.5 M NaCl at 30 Amp/ft².

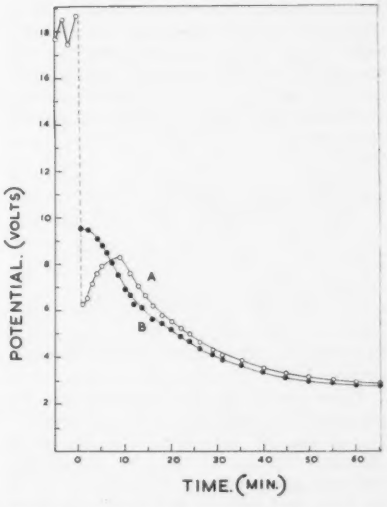

Figure 9—Introduction of platinum microelectrodes into lead (0.5 M NaCl, 30 Amp/ft²).

ent that at low potentials the thermodynamically favorable reaction is the formation of plumbous ions (Reaction 1). These ions cannot diffuse far into the electrolyte, however, owing to the low solubility of lead chloride which precipitates on the surface of the anode resulting in passivity ("mechanical").

As the initial crystals develop and further crystals nucleate, the paths of the electrolyte which permeate the crystals become more restricted and the rise in potential observed (Figure 3) is due largely to the increasing ohmic resistance. Similar results have been reported previously by Briggs and Wynne-Jones.[11] In addition, the lead chloride crystals will restrict the area of lead exposed to the electrolyte so that the current density and potential of the lead increases and eventually reaches a value where lead peroxide is thermodynamically stable (reaction 2). Oxidation of lead ions will occur, therefore, providing the chloride ion concentration in the vicinity of the lead surface is very small.

As the concentration of chloride ions increases by diffusion and migration a point will be reached where the lead peroxide will be penetrated by the chloride ions with the formation of lead chloride at the metal surface and detachment of lead peroxide. It is considered that this process of alternate formation of lead peroxide and lead chloride caused by alternate replenishment and depletion of hydroxyl ions and water dipoles and chloride ions is responsible for the fact that a stable lead peroxide film cannot be maintained in contact with a lead surface.

This situation is quite different, therefore, from the anodic behavior of lead in sulfuric acid. There, after initial formation of a very thin layer of lead sulfate at a potential which corresponds with the reversible $Pb/PbSO_4/H_2SO_4$ potential, the potential rises with the consequent oxidation of plumbous ions to lead peroxide.[12] Film growth of lead peroxide occurs only to a limited extent as the electrode process then becomes oxidation of water to oxygen at almost 100 percent efficiency. That lead peroxide formed in this way cannot be maintained in a chloride solution can be readily demonstrated. In addition, it can be shown that if a platinum microelectrode is inserted in a PbO_2/Pb anode, which has been formed in sulfuric acid, the lead peroxide is first detached by formation of lead chloride. This is accompanied by an increase in potential, and lead peroxide forms only subsequently.

The potential-time curves obtained with the lead-platinum bielectrode are characterized by a rise in potential to a maximum, which is associated with the initial evolution of chlorine from the platinum, and then a gradual fall to a steady state potential. Although the increase in potential observed is largely ohmic the increase in current density resulting from the deposition of lead chloride will cause the potential of the platinum to increase, since the platinum is in contact with the lead. It should, however, be emphasized that this situa-

tion will arise only if the lead chloride forms an adherent coating; at very low current densities it is possible to dissolve the lead anodically with very little increase in potential.

The platinum and the electrolyte permeating the crystals of lead chloride may be regarded as conductors in parallel. If the current is kept constant, the rate of formation of lead chloride will decrease as soon as the potential of the platinum is sufficiently high to cause chlorine discharge. These observations explain why the smaller the area of the platinum micro-electrode the higher the peak potential, as chlorine discharge will be determined by the potential of the platinum which depends in turn on the current density. Less current is required, therefore, for discharge of chlorine from a small wire and a larger proportion of the current will continue to form lead chloride with a consequent increase in potential. One role of the microelectrode is, therefore, to limit the extent of lead chloride formation. The decline in potential is clearly due to the formation of lead peroxide which is initiated at the microelectrode (Figure 5).

Although a stable lead peroxide film cannot be formed on a lead surface in the presence of chloride ions, owing to undermining of the peroxide by formation of lead chloride, there is no reason why peroxide should not deposit from a chloride solution onto platinum. Fleishmann and Liler[13] have shown, using lead acetate, that lead peroxide can readily nucleate and grow on a platinum anode and have suggested the following mechanism:—

$$OH^- - e = OHads \qquad (a)$$

$$Pb^{++} + OHads + OH^- - e = Pb(OH)_2^{++} \qquad (b)$$

$$Pb(OH)_2^{++} \rightleftharpoons PbO_2 + 2H^+ \qquad (c)$$

reaction (b) is considered to be rate determining.

Thus providing the potential of the platinum is sufficient, lead peroxide should deposit and remain stable on a platinum anode. It may be significant that the potential for oxidation of Pb^{++} to PbO_2 and for Cl^- to Cl_2 are approximately the same, so that nucleation of lead peroxide and discharge of chlorine may occur almost simultaneously. In considering the lead in the immediate vicinity of platinum it is suggested that two factors may be responsible for the stability of the lead peroxide—(a) nucleation and growth of lead peroxide on platinum, and (b) the oxidation of chloride to chlorine which occurs on platinum at a low overpotential (Figure 10).

If the oxidation of lead ions was the sole reaction at the platinum a stable film might form on the platinum, but it is difficult to see how the lead peroxide could extend over the lead surface and remain stable. The platinum could, however, act as a "chlorine valve" and provide a site where oxidation of chloride ions is kinetically easier than formation of lead chloride. The latter must occur by migration and diffusion of the lead and chloride ions through the interstices of the lead chloride and lead peroxide crystals. It is apparent from Figure 3 that the latter process requires a far higher potential than oxidation of the chloride ions on platinum. The combination of (a) and (b) will result, therefore, in the nucleation of lead peroxide on the platinum at the lead/platinum interfaces. Further peroxide can now deposit on the initial nuclei and extend into the lead chloride owing to the ability of the platinum electrode to prevent the potential rising to a value where the chloride ions can penetrate the lead peroxide. An analogy is the ability of the chloride ions to penetrate the anodic oxide on titanium which occurs only if the oxide/electrolyte potential is greater than ~ 12-14 V. This potential usually cannot be exceeded if the surface of the titanium is in contact with platinum.

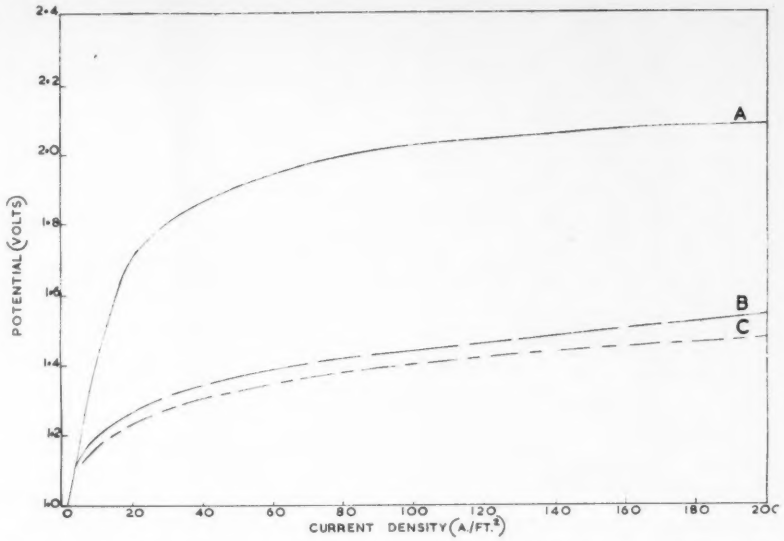

Figure 10—Potential-current density curves: "A" for a platinum electrode, "B" for a platinum microelectrode in lead and "C" for lead peroxide on a lead-platinum bielectrode.

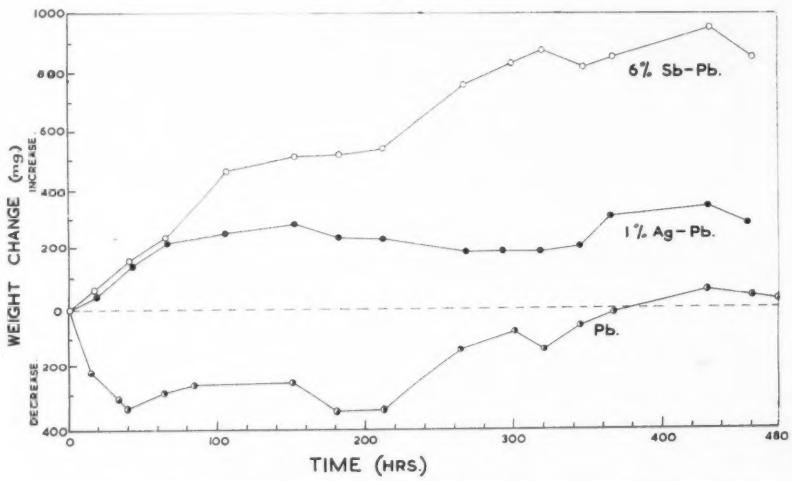

Figure 11—Change in weight of lead, 1 percent Ag/Pb, 6 percent Sb/Pb containing platinum microelectrodes (2 X 0.020" dia. at position "a") in artificial sea water at 30 Amp/ft².

Wheeler[14] considers that the sole function of the platinum is to make contact between the lead and lead peroxide which appears to be substantiated by the fact that removal of the platinum results in an immediate increase in potential (Figure 8). A further experiment which appears to support this view is that if, after forming peroxide, the bielectrode is then arranged so that the platinum is above and the lead below the level of the electrolyte the immersed lead peroxide remains stable on the lead surface during further electrolysis.

Although the platinum is undoubtedly in contact with the lead and lead per-

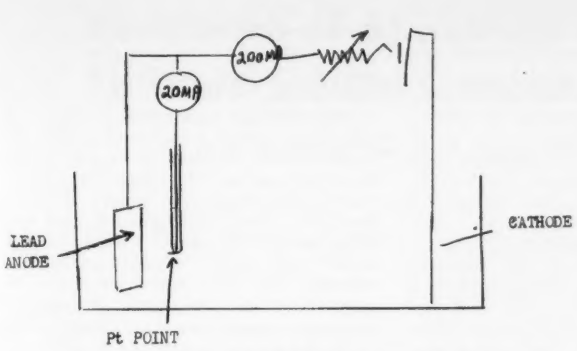

Figure 12—Platinum point in parallel with lead anode.

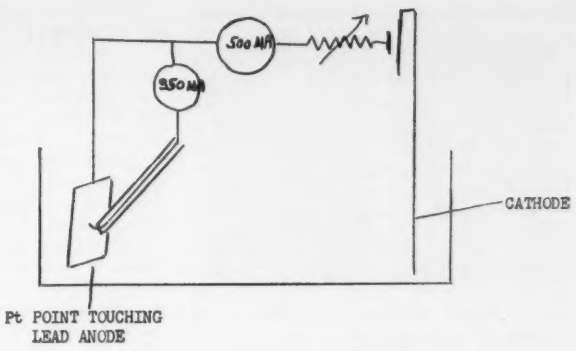

Figure 13—Platinum point touching lead anode.

oxide it is considered that this is not the cause but the consequence of the ability of the platinum to cause nucleation of lead peroxide (Figure 5) and to oxidize the chloride ion at a low overpotential. The initial lead peroxide crystals apparently form around the platinum and lead peroxide then extends over the *surface* of the lead chloride without being in contact with the lead substrate. At this stage, removal of the platinum will clearly result in an increase of potential. After more prolonged electrolysis, however, all the lead chloride is converted to peroxide which is then in direct contact with the lead. The electrode can then function without the presence of platinum for a limited period.

To summarize, it is considered that the role of the platinum microelectrode is (a) to limit the initial formation of lead chloride, (b) to oxidize plumbous ions to lead peroxide which remains stable on the platinum surface and then extends into the adjacent lead chloride, and (c) to act as a "chlorine valve" so that lead chloride formation is prevented during operation. Further work on the formation of lead peroxide from chloride electrolytes on lead and platinum is in progress and will form the subject of a future paper.

Cathodic Protection

Laboratory trials and service tests have indicated that platinum-lead bielectrodes may have an important application as a comparatively inexpensive anode for cathodic protection and other electrolytic processes. Laboratory tests[4] have shown that a 1 percent Ag-Pb alloy, which without platinum is limited to a current density of 10 to 15 Amp/ft², containing platinum microelectrodes can be used satisfactorily at 200 Amp/ft². In practice, platinum lead bielectrodes have now been in use for eighteen months at 25 Amp/ft² in sea water for protection of marine structures, and appear to be functioning satisfactorily. Service tests are being carried out in sea water moving at 6 ft/sec. at 25, 50, 100, and 200 Amp/ft².

In conclusion it should be observed that the sudden failure that has been experienced with lead alloys after prolonged electrolysis may be the result of growth of lead peroxide and the development of stresses in the film owing to the volume of lead peroxide being greater than the lead converted. A characteristic of many lead anodes (whether they contain platinum or not) is the formation of surface blisters indicating that the peroxide is under high compressional stress. It is possible, therefore, that after some time the peroxide may tend to pull away from the lead and crack so that the electrolyte has access to the lead surface. Under these circumstances lead chloride will continue to form with consequent increase in the anode resistance. This situation is unlikely to arise if the lead is in contact with a platinum microelectrode.

Acknowledgment

Acknowledgments are made to M. Giles of the Metal and Pipeline Endurance Co. Ltd. for carrying out the experiments and to J. G. Gerrard, Chief Corrosion Engineer, for sponsoring this work.

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DISCUSSION

Comments by J. T. Crennell, Central Dockyard Laboratory, H. M. Dockyard, Portsmouth, England:

My colleague, Mr. Wheeler, who has recently retired, was mainly responsible for our work on lead anodes for cathodic protection. He proposed the use of an alloy containing 1 percent silver which has proved successful.

Regarding the use of a platinum tack, as described by Shreir and Weinraub,* we made a number of laboratory tests as a result of which Mr. Wheeler suggested that the function of the "tack" was to maintain a low-resistance contact between the shell of lead dioxide and the underlying metal. This he referred to in a letter to the Editor of "Chemistry and Industry," Jan. 17, 1959, p. 75.

I will not go into details of the many tests we made of this hypothesis, but you may be interested in one which seems to me very convincing.

A pure lead anode *(without* platinum tack) which had formed a lead dioxide skin but had subsequently ceased to work properly, requiring a high driving voltage for a small current, was in circuit in a sea water bath. In parallel with it, and separately metered, was a small platinum point projecting from a sealed glass tube carrying the connecting wire. (See Figure 12.) The platinum point was taking a current of 20 mA, the lead anode about 200 mA, with a cell voltage of 3.6 V.

The platinum point was then brought up to contact the lead dioxide surface (Figure 13) below the liquid. Immediately the current in the platinum-point meter jumped to 350 mA, and the total current to about 500 mA. (There was some drop in cell voltage.) This behavior could be repeated at will.

This can only mean that the (external) Pt point was providing a contact to the lead dioxide anode of much lower resistance than that through the underlying lead, a function we believe also to be performed by a platinum spine inserted into the lead.

Reply by L. L. Shreir:

Mr. Wheeler has suggested that the sole function of the platinum is to make electrical contact between the lead and the lead peroxide which is insulated by a film of high resistance, which implies that the entire current passes through the platinum from the lead to the shell of lead peroxide. This model is attractive for its simplicity, and it might appear that the views expressed in my article lead to a model which is unnecessarily complicated. Indeed, the effect of the withdrawal and introduction of the platinum micro-

* Shreir and Weinraub. *Chem. & Ind.*, 1326 (1958).

electrode (Figures 8 and 9) and the experiment described by Mr. Crennell appear to indicate that the platinum is, in fact, acting as a short circuit.

The present work and subsequent studies have indicated, however, that the electrode processes occuring in this system are highly complex, and it is considered unlikely that any one mechanism will be capable of explaining the over-all phenomenon. It is relevant to consider some of the possible stages in the conversion of the initial Pb - Pt bielectrode to a completely passive Pb/PbO_2 - Pt anode. These can be enumerated as follows:

(a) Formation of passive film of lead chloride

(b) Nucleation of lead peroxide at the Pb - Pt interface and simultaneous discharge of chlorine at platinum

(c) Propagation of lead peroxide, from the platinum, over the surface of the lead chloride formed initially

(d) Gradual conversion of underlying lead chloride to peroxide which forms in direct contact with the lead

(e) Growth of lead peroxide to a limiting thickness

(f) Passivity, electron current sole process at anode.

Even this may be an oversimplification, and the effect of chlorine in the electrolyte may have some effect.

Considering stage (a), although it is apparent that the platinum will limit the extent of the growth of the initial lead chloride film (Figures 4, 6 and 7), prevention of lead chloride formation by the platinum is essential during all other stages of the process. There is definite evidence that stage (d) occurs and that the lead and peroxide are in actual electrical contact. This can be demonstrated by fully forming a bielectrode, raising the platinum above the electrolyte level and then removing the platinum, when the anode will function satisfactorily for some time, showing that the lead and lead peroxide are in contact. However, should a discontinuity be produced, formation of lead chloride at the Pb/PbO_2 interface occurs rapidly with a consequent rise in potential. Thus, one role of the micro-electrode is to prevent lead chloride forming on the lead surface.

With regard to stage (b), Figure 5 shows how the lead peroxide nucleates only at the platinum and then extends over the surface of previously formed lead chloride. In this connection it should be observed that lead peroxide cannot be undermined from a platinum surface by an alternative electrode process as occurs on a lead surface. Removal of the platinum at this stage will clearly result in the effect shown in Figure 8, and will occur even if the anode is fully formed, as the removal of the platinum will expose the lead to the electrolyte.

Similarly, the introduction of platinum into lead coated with lead chloride will cause immediate nucleation of lead peroxide at the platinum, and a consequent fall in potential. A similar effect will be produced if the platinum is polarized, as in Mr. Crennell's experiment.

It is considered, therefore, that the platinum provides contact between the lead and the lead peroxide by *preventing* lead chloride formation at the lead interface and by acting as a nucleus for deposition of lead peroxide which subsequently propagates over the surface.

Any discussion of this article not published above will appear in June, 1961 issue.

Resistance of Aluminum Alloys To Underground Corrosion*

By D. O. SPROWLS and M. E. CARLISLE, JR.

Abstract

This paper is a summary of field test data and service experience on aluminum underground. The effect of variations in soil composition and the relative performance of different alloys are discussed. Cathodic protection, protective coatings, stray currents, and galvanic effects are considered. Experience with several aluminum pipe lines is related. 6.4.2, 4.5.3, 3.6.9, 3.6.6, 8.9.3

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Introduction

WHEN APPRAISING a metal's general resistance to corrosion, soil is an important environment to consider because of the large number of metal structures buried underground or in contact with the surface of the ground. Unfortunately, this common medium is one of the most difficult to evaluate because of the wide variations in chemical and physical characteristics of soils and in their corrosivity to metals. Also, there has been no general agreement as to which criteria are the most useful in predicting metal performance underground.

Owing to this wide variation in corrosiveness of soils, any metal considered for this field will naturally be used with caution until experience has shown the conditions under which it will require protection. In certain environments where mild steel requires a protective coating, bare aluminum alloys have performed impressively. It has been found that aluminum is well suited for several types of surface and underground pipe lines in the petroleum, mining and farming industries, as well as for many structures such as lighting standards and fence posts. Engineers are naturally interested to know about the experience that has been recorded with aluminum. The purpose of this paper is to summarize some available field test data and service experience for aluminum alloys. Consideration is given also to stray current corrosion and galvanic corrosion in soil environments and to the means of avoiding these problems.

Field Tests

Comparison of Different Soils

Several important factors in the makeup of a soil affect underground corrosion: moisture content, degree of aeration, concentration of soluble salts, hydrogen ion concentration, and apparent specific gravity. Localized variations in certain of these factors cause differences in solution potential that stimulate electrochemical corrosion at the anodic areas. Corrosion underground may also be accelerated by the presence of stray electrical currents or by galvanic currents which result from connecting the structure with more cathodic metals. The complexity of the problem prevents the accurate prediction of the extent of corrosion to be expected of buried metallic structures. It is anticipated, however, that a study of these factors in conjunction with each test and service experience will lead to broader understanding of the problem and to the formulation of certain rules to govern the use of aluminum structures underground.

One of the earliest soil tests of aluminum alloys was included in the National Bureau of Standards investigation[1] in which panels of 0.062 inch thick sheet of three alloys of aluminum, along with other metals, were buried in five different soils for a period of ten years. Steel samples, also 0.062 inch thick, were severely corroded at all five locations and completely destroyed at three of them. The aluminum alloys developed severe localized attack and perforations at four of the five test sites, but in the fifth location they were scarcely affected. The fifth location was a tidal marsh in which steel was completely destroyed and which, from a consideration of the low pH, low resistivity and high concentration of water soluble salts would be considered likely to be corrosive.

The results of five-year exposures[2] of aluminum sheet (0.125 inch) and 1 inch diameter tube samples buried in five different soils are summarized in Table 1. At one location where the soil consisted of clay with some glacial till, there was no corrosion of the aluminum. In three locations, there was scattered pitting ranging from 30 to 86 mils maximum depth. The fifth location was a cinder embankment which caused severe general attack. It will be noted that in every location the total corrosion of the steel samples, as expressed in terms of cubic inches per square inch per year, was much greater than that of aluminum.

In an investigation conducted a number of years ago by Alcoa Research Laboratories, samples of sheet, 0.064 inch x 3 inch x 9 inch in size, of several alloys of aluminum and mild steel were buried in four different soils. The results of tensile tests performed on these panels after nine to twelve months exposure are given in Table 2. None of the more corrosion-resistant alloys showed any appreciable loss in strength in these relatively short exposure periods. Although widely different corrosion rates were observed on the less resistant Al-Cu type aluminum alloy, 2017-T3, it did not appear that the corrosion effects could be correlated with the soil compositions and resistivity measurements shown in Table 2.

The results of these several tests indicate that unprotected aluminum alloys may be virtually unaffected under some conditions and severely corroded in certain other types of soils. Although the available information indicates generally that soils which are aggressive to steel are likely also to be aggressive to aluminum, exceptions which favor aluminum have been noted. Attempts to correlate the behavior of aluminum with soil analyses have been unsuccessful. Additional experience is needed to learn the characteristics of the soil at a given location

TABLE 1—Resistance to Corrosion of Commercially Pure Aluminum Buried Five Years in Five Different Types of Soil[1, 2, 3, 4]

Soil	Maximum Pit Depth, Mils		Corrosion Rate $in^3/in^2/yr \times 10^{-3}$	
	Al Sheet	Al Tube	Al Sheet	Steel Sheet
Clay with glacial till (Rothamstead)	Nil	Nil	0.01	0.79
Moist London clay (Pitsea)	39	33	0.02	1.04
Salt marsh, moist (Benfleet)	66	41	0.12	1.33
Moist clay with gypsum (Gotham)	86	63*	0.01	0.33
Cinder embankment, well drained (Corby)	Perforated	..	0.77	1.98

[1] Test samples of aluminum were exposed in triplicate in the form of 15 inch x 10 x 1/8 inch sheet panels and 15 inch long x 1 inch diameter x 1/16 inch wall tubes. The mild steel sheet panels were 15 inches x 10¼ inches x 5/16 inches. All samples were buried in 2 ft. deep trenches.

[2] Pit depths were measured using a dial gauge fitted with a fine point.

[3] Corrosion rates were calculated from weight loss data.

[4] Data were obtained from Reference 2.

* In this environment a special group of twelve additional tubes was exposed: of the total of fifteen two were perforated, two were not pitted, and the remainder were pitted to various depths.

★ Submitted for publication February 25, 1960. A paper presented at the 16th Annual Conference, National Association of Corrosion Engineers, Dallas, Texas, March 14-18, 1960. This paper was also published in *Proceedings: Short Course on Process Industry Corrosion, Ohio State University*, Sept. 12-16, 1960, NACE, Houston, Texas.

that are most significant in predicting its corrosivity.

Performance of Various Aluminum Alloys

Because the resistance of aluminum and aluminum alloys to corrosion is dependent upon an oxide film, the initiation of corrosion occurs at weak points in the film, and the characteristic type of attack of most alloys is pitting. This has been observed to be the case in soils as well as in other natural environments. It is anticipated that the decreasing rate of penetration with time, which has been observed in the atmosphere and in fresh waters, may also be characteristic of aluminum in soil corrosion. Data which indicate that this may be the case are discussed later in this section.

Concern about the possibility of perforation of thin sections as a result of pitting corrosion led to the development of alclad aluminum alloys. Alclad products consist of an aluminum alloy core covered on one or more surfaces with one or more layers of corrosion-resistant aluminum or aluminum alloy. The thickness of the coating on each surface is typically 2½ to 10 percent of the total section thickness. The aluminum alloy coating and core combinations usually are selected so that in corrosive environments the coating is anodic to the core and, hence, exerts electrochemical protection over exposed areas, such as cut edges, scratches, or spots uncovered by corrosion or abrasion. Although behavior in soils is unpredictable, it has been observed that the performance of the alclad alloys was outstanding in every instance. The majority of the non-clad aluminum alloys, with the exception of the aluminum-copper (and the aluminum-zinc-magnesium-copper alloys), may be placed in a gronp with approximately similar resistance to soil corrosion. The exceptions noted are the high-strength, heat-treated alloys common in aircraft construction. The composition and typical tensile properties of the alloys to be discussed are given in Table 3.

The superior performance of the alclad type of alloy is shown by the data in Table 4 obtained in a test in which a number of test panels of 0.064 inch thick sheet were buried on a greenhouse bench in soil that was watered daily. The panels were removed and tested after periods of five and twenty-two months. It will be noted that the relatively shallow corrosion of the Alclad 3003-H14 panels, which was limited to the thin cladding layer, had not resulted in any loss in the strength of the sheet.

Data obtained for a number of aluminum alloys buried four and a half years in the yard of the Alcoa Research Laboratories at New Kensington, Pennsylvania, and published previously by Mears[3] are given in Table 5. With the exception of alloy 2017-T3, the non-clad alloys performed similarly, although there ap-

TABLE 2—Resistance to Corrosion of Several Aluminum Alloys Buried at Various Geographic Locations[1]

Alloy	Upper Straits, Michigan 9 Months		Portland, Indiana 9 Months		Detroit, Michigan 9 Months		Point Judith, Rhode Island 12 Months	
	Percent Loss in T.S.	Visual[2]	Percent Loss in T.S.	Visual	Percent Loss in T.S.	Visual	Percent Loss in T.S.	Visual
1100-H14	1	e	1	b, c	1	b, f	0	b, e
3003-H14	1	c	8	b, c	1	b, f	1	b, e
5052-H34	0	b	0	b, e	3	b, f	1	b, e
6053-T6	2	a	1	b, e	5	b, f	0	b
2017-T3	0	b	6	b, e	25	g	67	g
Alclad 2024-T36	1	a	1	b	0	b, c	0	b, c
Mild Steel	2	b	8	c, f	9	c	26	c, g
Soil Analyses								
pH of Air Dried Soil	7.1		5.8		7.4		5.5	
Resistivity: -Ohm-Cm	1560		3550		9260		2095	
Composition of Water Extract (Mg-Eq. per 100 g/soil)								
Na + K as Na	1.31		0.10		0.10		1.03	
Ca	4.37		0.01		0.03		0.03	
Mg	1.45		0.05		0.05		2.56	
CO_3	0.00		0.00		0.00		0.00	
HCO_3	6.3		0.23		0.27		0.27	
Cl	0.15		0.00		0.00		0.18	
SO_4	1.15		0.10		0.15		0.48	

[1] Exposed as 0.064 inch thick sheet panels.
[2] Code for visual examination:
a — No appreciable attack
b — Etching or superficial pitting
c — Local areas of shallow attack
d — Local incipient exfoliation
e — Many small pits
f — A few relatively deep pits
g — Severe general pitting

TABLE 3—Composition and Typical Tensile Properties of Aluminum Alloys Under Discussion

Alloy	Nominal Composition, Percent						Temper	Tensile Strength, psi	Yield Strength (0.2 Percent Offset), psi	Elongation—Percent in 2 Inch	
	Cu	Si	Mn	Mg	Cr	Zn				Sheet Specimen 0.064 Inch	Round Specimen 0.50 Inch Dia.
Wrought Alloys											
1100	99.0 % Minimum Aluminum						H14	18,000	17,000	9	20
3003	...	..	1.2	..	...	..	H14	22,000	21,000	8	16
3003	...	..	1.2	..	...	..	H18	29,000	27,000	4	10
Alclad 3003[1]	...	..	1.2	..	...	..	H14	22,000	21,000	8	16
5052	...	..	..	2.5	0.25	..	H34	38,000	31,000	10	14
2017	4.0	..	0.5	0.5	...	..	T4	62,000	40,000		22
Alclad 2024[2]	4.5	..	0.6	1.5	...	..	T3	65,000	45,000	18	..
Alclad 2024[2]	4.5	..	0.6	1.5	...	..	T36	67,000	53,000	11	..
6053	...	0.7	..	1.3	0.25	..	T6	32,000	37,000	..	13
6061	0.25	0.6	..	1.0	0.25	..	T6	45,000	40,000	12	17
6063	...	0.4	..	0.7	...	..	T5	27,000	21,000	12	..
6063	...	0.4	..	0.7	...	..	T6	35,000	31,000	12	..
Alclad 6063[1]	...	0.4	..	0.7	...	..	.....	.....	.....	12	..
Cast Alloys											
43	...	5.0	..	..	...	..	—F	19,000	8,000	..	8
112	7.0	..	..	..	...	1.7	—F	24,000	15,000	..	1.5
B214	...	1.8	..	3.8	...	..	—F	20,000	31,000	....	2.0
B605	...	..	..	..	...	5.5	....	.....	.....	..	..

[1] Alclad coating is alloy 7072 (1 percent zinc).
[2] Alclad coating is alloy 1230 (99.3 min. percent aluminum).

peared to be a slight advantage for alloys 5052-H34 and 6053-T6. The 2017-T3 was pitted rather extensively and exhibited a resistance similar to that of the mild steel. The excellent performance of Alclad 2024-T36 was in sharp contrast. It also is noteworthy that, in general, the aluminum alloys were attacked more in the poorly aerated wet location than in the well-drained location, less than 100 feet away; the steel samples, on the other hand, showed the reverse tendency.

Recently, an eight-year burial test of pipe specimens was completed in the same vicinity as the test just described. Five foot lengths of 1¼ inch Schedule 40 pipe and two foot lengths of 6 inch Schedule 40 pipe containing butt welded joints were buried in trenches three feet deep. The trenches were located in well-drained, light brown clay on a gentle slope adjacent to a small spring-fed stream. A list of the various aluminum alloys and comparison metals included is given in Table 6. Duplicate sets of specimens were buried and these were removed for examination at different periods and re-exposed for a total of seven or eight years. Visual inspection of all specimens disclosed more corrosion of the seven year specimens; consequently, these were sectioned instead of the eight year set for microscopic examination. The depth of penetration was determined by microscopic examination of metallographic sections taken through several pits of maximum size as judged by visual examination. The maximum pit depths after two, four and seven or eight years are given in Table 6.

Graphs of maximum pit depth versus exposure time are shown in Figure 1. The general similarity in behavior of the non-clad aluminum alloys is shown. The data indicate that the rate of penetration under these conditions of discontinuous exposure decreased with time beginning at about four years. Limited data on alloys 6063-T6 and B214 indicate that this trend may also hold for continuous exposures. However, it might be debated which is the more severe—a continuous exposure such as a buried pipe line would probably experience or discontinuous exposure such as these test specimens received.

The contrast between the 6063-T6 and the outside Alclad 6063-T6 was marked, again illustrating the superiority of the alclad type of alloy in providing the best resistance to pitting. This is shown also by the photomicrographs in Figures 2 and 3. A photograph of the welded 6 inch outside Alclad 6063-T6 pipe and a cross-section of the weld are shown in Figures 4 and 5. The alclad coating on the 1¼ inch outside Alclad 6063-T5 pipe also was very effective in protecting the core alloy, and the surface showed many broad areas of shallow attack of the cladding similar to that on the 6 inch pipe (Figure 4). However, it was found that three or four small, comparatively deep pits had developed in the 6063-T5 core in one of the largest areas where the cladding had been consumed. The maximum penetration observed was 73 mils. The alclad coatings on these samples of pipe were relatively thin, approximately 4 percent of the wall thickness. A thicker alclad coating would assure a longer life of the cladding before pitting of the core alloy would commence.

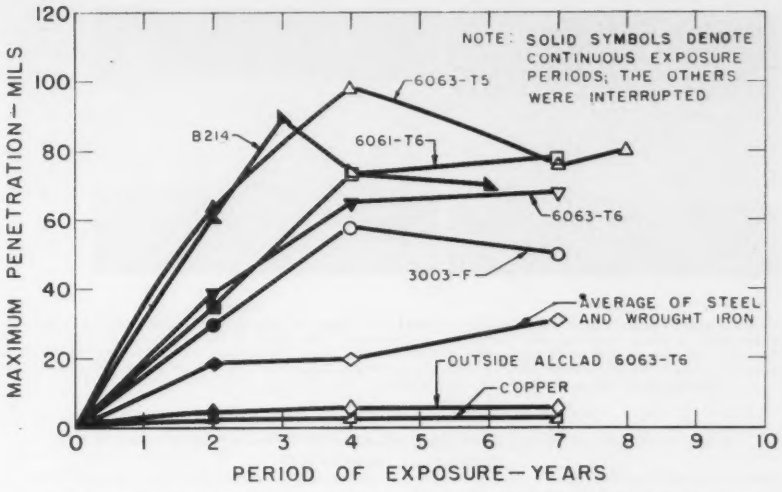

Figure 1—Pit depth-time curves for aluminum alloy pipes buried at New Kensington, Pa.

TABLE 4—Resistance to Corrosion of Aluminum Alloys Buried 22 Months in Soil On a Greenhouse Bench[1, 2]

Alloy	Percent Loss in Tensile Strength		Maximum Depth of Pits, Mils	
	5 Months	22 Months	5 Months	22 Months
5052-H34	0	11	0.7	Perforated
3003-H14	0	8	4.1	18
Alclad 3003-H14	0	0	1.5	5.1*

[1] Exposed as 0.064 inch thick sheet panels.

[2] The pH of the soil was 8.6 and the composition of a water extract in Mg-Eq./100 gm. of soil was as follows: Na + K, as Na, 0.91; Ca, 11.65; Mg, 1.28; CO_3 0.48; HCO_3 1.42; Cl, 0.11 SO_4 6.78.

* Penetration of pitting into the 3003-H14 core alloy was prevented by the electrochemical protection afforded by the 5 mil cladding layer.

TABLE 5—Resistance to Corrosion of Various Aluminum Alloys Buried 4½ Years at New Kensington, Pennsylvania[1, 2]

Alloy	Well Drained Location			Poorly Drained (Wet) Location		
	Percent Loss in T.S.	Maximum Pit Depth, Mils	Visual Examination[3]	Percent Loss in T.S.	Maximum Pit Depth, Mils	Visual Examination
1100-H14	1	1.7	b	7	28.0	b, e, f
3003-H14	0	16.3	d, f	3	25.0	b, e, f
5052-H34	0	0.7	b	0	14.0	b, f
6053-T6	0	0.7	b	0	15.0	b, f
Alclad 2024-T36	0	1.3*	c	1	2.8*	c
2017-T3	20	38.0	g	41	31.0	g
Mild Steel	27	Perforated	g	17	19.0	b, g
60/40 Brass	6	8.9	b	7	5.6	b

[1] Exposed as sheet panels 0.064 inch x 3 inch x 9 inch buried at a depth of two feet.

[2] The pH of the soil was 5.4 and an analysis of a water extract of the soil was as follows; expressed in Mg-Eq./100 g. of soil:

Na + K as Na, 0.05; Ca, 0.15; Mg, not determined; CO_3 0.00; HCO_3, not determined; Cl, 0.0: SO_4, 0.46. See also the analyses appended to Table 6.

[3] Code for visual examination:

a — No appreciable attack
b — Etching or superficial pitting
c — Local areas of shallow attack
d — Local incipient exfoliation
e — Many small pits
f — A few relatively deep pits
g — Severe general pitting

* Attack limited to the alclad coating which had given electrochemical protection to the 2024-T36 core.

Tensile tests were made on a 24-inch length of both the 6061-T6 alloy and the mild steel pipe after the seven year exposure. It is interesting to note that the rather general pitting of the 6061-T6 pipe (similar to that shown for the unprotected pipe of 6063-T5 in Figure 6) had caused only a small loss in ultimate tensile strength. The ultimate tensile strength of the exposed 6061-T6 pipe was 42,000 psi, with typical and guaranteed minimum values for this alloy being 45,000 psi and 38,000, respectively. The ultimate tensile strength of the exposed mild steel pipe was similar at 45,000 psi.

Cathodic Protection

Cathodic protection of aluminum alloys, unlike steel, must be controlled to avoid over-protection with resultant alkaline attack of the aluminum. It is beyond the scope of this paper to present a detailed discussion of cathodic protection.

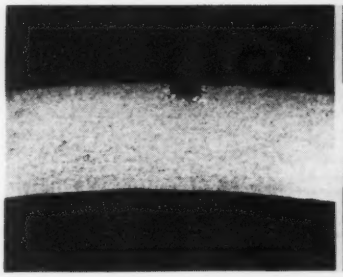

Figure 2

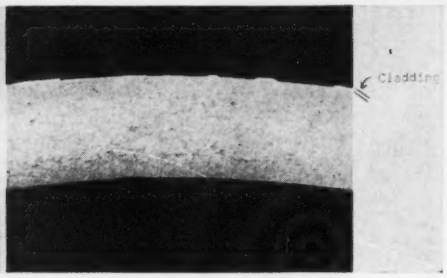

Figure 3

Cross-sections through 6-inch diameter pipe of 6063-T6 (Figure 2) and outside Alclad 6063-T6 (Figure 3) alloys after 7 years burial at New Kesington, Pennsylvania. The depth of the pit shown in Figure 2 was 52 mils; the deepest pit measured on this sample was 68 mils. Penetration of pitting into the 6063-T6 alloy core of the outside Alclad 6063-T6 pipe was prevented by the electrochemical protection afforded by sacrificial corrosion of the 6 mil thick cladding layer. Keller's etch, approximately 2.5X.

TABLE 6—Depth of Pitting in Pipe Samples Buried Seven or Eight Years at New Kensington, Pennsylvania

Alloy	Maximum Pit Depth, Mils		
	2 Yrs.	4 Yrs.[5]	7 Yrs.[5]
1¼" Schedule 40 Pipe (0.140" Wall)			
3003-F	30	58	50
3003-F Coated and Wrapped[3]		No Corrosion	
6061-T6	35	73	78
6063-T5	64	98	76[4]
6063-T5 Coupled to Anode of Al Alloy B605	..	..	22 (8 yr.)
Outside Alclad 6063-T5	5	6	6[1]
B214 Alloy Cast Pipe Cap	62	73	70 (6 yr.)
Wrought Iron	89 (3 yr.) 25[2]	19[2]	33[2]
Mild Steel	13[2]	21[2]	29[2]
Malleable Iron Pipe Cap	..	..	40
Galvanized Steel	5	4	12
Copper	3	3	3
85/15 Red Brass	2	4	4
6" Schedule 40 Pipe (0.280" Wall) Welded with 4043 Alloy Filler	**2 Yrs.**	**4 Yrs.**	**7 Yrs.[5]**
6063-T6	39	65	68
Outside Alclad 6063-T6	5	6	6

[1] Although almost all of the attack was confined to the cladding layer, three or four small diameter pits, the deepest of which was 73 mils, were found at sites where the cladding had corroded away.
[2] Micrometer measurements of the corroded pipe indicated losses in thickness by general corrosion to be not appreciable after 2 years, 5 mils after 4 years and 8 mils after 7 years.
[3] Coating system consisted of two hot coats of a pipe line enamel to a total thickness of 1/16 inch, one wrap of Fiberglass pipe wrap, and one wrap of heavy Kraft paper.
[4] Depth of attack in the 8 yr. (2 yr. + 6 yr.) specimen was 80 mils.
[5] Discontinuous exposure periods: 1¼ inch pipe—4 yr. = 2 + 2 yr.; 7 yr. = 2 + 2 + 3 yr.—6 inch pipe—7 yr. = 4 + 3 yr.
[6] Analyses of soil samples: No. 1 at location of 1¼ inch pipes and No. 2 at location of 6 inch pipes.

Location	Resistivity Ohm-Cm	pH	Composition of Water Extract (Mg-Eq./100 g. of Soil)						
			Na + K (as Na)	Ca	Mg	CO_3	HCO_3	Cl	SO_4
No. 1	3,500	6.1	0.61	N.D.	0.29	0.00	0.24	0.38	0.97
No. 2	25,000	4.7	0.47	N.D.	0.00	0.00	0.08	0.01	0.51

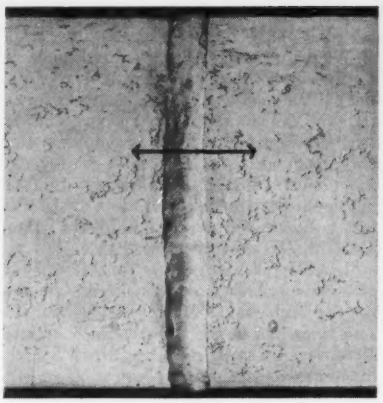

Figure 4

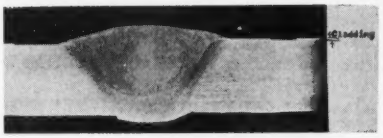

Figure 5

Figures 4 & 5—Photograph and cross-section of joint welded with 4043 filler wire in outside Alclad 6063-T6 pipe 6 inches in diameter after 7 years burial at New Kensington, Pennsylvania, and subsequent chemical cleaning. The arrow in Figure 4 indicates the location of the cross-section shown in Figure 5. The broad, shallow areas of sacrificial corrosion evident in the cladding illustrate the typical performance of an alclad alloy with penetration of the core alloy being prevented by the electrochemical protection afforded by the more anodic cladding alloy. Magnification of Figure 4 is approximately 0.3X; magnification of Figure 5 is approximately 2X (Keller's etch.)

However, in the pipe test described above there was included a five foot length of 1¼ inch pipe of alloy 6063-T5 to which an anode of cast aluminum alloy B605 was connected. The exposure of this pipe was not disturbed until completion of the eight year period when it was removed from the ground. Potential measurements using a copper-copper sulfate reference electrode were made at various intervals during the exposure, and it was noted that the polarized potential of the pipe ranged from —1.1 V at the beginning to —0.9 V at the end of the eight years. The potential of the unprotected pipe fluctuated widely, but generally was of the order of —0.6 to —0.8 V. The high degree of protection afforded by the B605 anode (Al-5.5 Zn alloy) is strikingly shown by the photograph in Figure 6.

Additional experience such as is being obtained on the Alcoa gas-gathering line at Point Comfort, Texas, and in other service installations[4,5] is required to determine optimum practice for cathodic protection. For a tentative guide, it is suggested that the polarized potential of the pipe be maintained between —0.9 and —1.2 V.

Protective Coatings

It has been shown in a number of instances that protective coatings may be employed to insure an adequate resistance to corrosion of aluminum in contact with soil. An example of the excellent protection afforded by a typical pipe coating and wrapping system is shown in Figure 7.

Data are assembled in Table 7 to show the protection afforded by various types of coatings to aluminum alloys exposed four and a half to eleven and a half years at New Kensington, Pennsylvania. These data were obtained at the same sites as the information given in Table 5. The chemical conversion-type coating (Alrok No. 13) and the Alumilite 204 anodic finish afforded some protection to 6053-T6 alloy in the four and a half year exposure to marshy soil, but the Alumilite 202 (a slightly thinner oxide coating than Alumilite 204) anodic finish provided only slight protection to alloy 3003-H18 buried for eleven and a half years. It seems doubtful that either the chemical coating or the anodic coatings would afford significant protection when used alone, but they are very effective as surface treatments for paint coatings. Panels of alloys 1100-H18, 3003-H18, 6053-T6 and 2017-T3 sheet and sand-cast 43 alloy when given an Alrok No. 13 treatment followed by a zinc chromate primer plus aluminum paint system were in excellent condition after eleven and a half years in both the well-drained and the poorly drained test sites. A proprietary phosphoric acid treatment also appeared to be a satisfactory surface preparation for painting.

A subsequent ten year exposure completed at a test site provided by the Sun Oil Company in a swamp with high organic content in Hudson Township, Ohio, tended to corroborate the above results and provided data on additional coatings. It was shown that a zinc chromate primer plus aluminum paint system

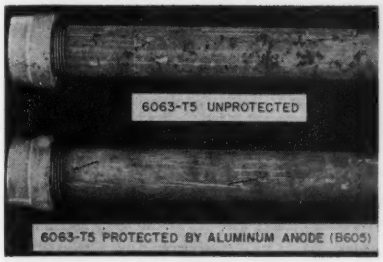

Figure 6—Ends of 5 ft. lengths of 6063-T5 alloy 1¼-inch diameter pipe with B214 alloy caps buried 8 years at New Kensington, Pennsylvania and subsequently chemically cleaned. Only a few very small pits were present on the cathodically protected pipe in contrast to the general pitting on the unprotected pipes of 6063-T5 and the other aluminum alloys. The maximum depth of pitting in the protected pipe was only 22 mils in comparison to 80 mils for the unprotected pipe.

applied to panels of 6061-T6 sheet provided good protection to the metal but suffered extensive blistering even with an Alrok coating surface preparation. A vinyl resin system and heavy bodied bituminous coatings applied hot or cold, on the other hand, showed no evidence of breakdown. A metallized coating of 99.8 percent aluminum when applied to cast panels of aluminum alloys 43 and 112 provided excellent protection by sacrificial corrosion of the metallized coating in the same manner as the cladding on a conventional alclad product. Therefore, for products that cannot be fabricated in the alclad form, the application of a metallized coating of high purity aluminum or a suitable alloy such as 4043 or 7072 would be expected to provide considerable protection against even the most aggressive environments.

Figure 7—Shows an area of the coated and wrapped 3003-F alloy 1¼-inch diameter pipe with the coating stripped off to reveal the uncorroded surface of the pipe. After seven years burial at New Kensington the only deterioration of the coating noted was some shallow cracks that extended only as deep as the Fiberglass wrap.

Service Experience

Most of the important service experience with aluminum alloys in contact with soil has been in oil and gas flow lines and gathering lines. Much of this experience has been uncontrolled, but several larger lines have merited rather careful collection of data and inspections.

Flow Lines

A 3,500 foot long flow line of 4 inch Schedule 40 alloy 6063-T6 pipe was laid in Matagorda Bay, Texas, in 1950 as part of the gas supply system for Alcoa's Point Comfort, Texas, smelter. One-half of this line is completely unprotected while the remainder is coated and wrapped in a conventional manner. When part of the unprotected line was lifted for inspection after a period of eight years, a portion of it was covered with a thick, gelatinous coating of mud on top of a very uniform and continuous layer of marine formations. Removal of these materials revealed a pattern of only superficial etching of the surface. Except for the etching, this portion of the pipe appeared to be in the same condition as on the day of installation.

A 4 inch Schedule 40 welded 6063-T6 alloy crude oil pipe line about 8,000 feet long was laid in May, 1948, on the bank of the Intracoastal Canal in Southern Louisiana. The aluminum line was buried unprotected in ground slightly higher than the surrounding marsh in an area where unprotected steel pipe had developed leaks in two years and required replacement in five years. No appreciable external corrosion had been discovered up to July, 1950, (26 months) at which time the line was moved to another location.

An above ground flow line was laid unprotected in Louisiana marsh country in 1954. In some locations where the swamp is very wet, the line has sunk completely from view. A 1958 inspection (after more than four years of exposure) indicated no appreciable external corrosion.

Gathering Lines

One of the first permanent aluminum pipe lines was a five mile long 6 inch Schedule 40 alloy 6063-T6 sour crude

TABLE 7—Protection Afforded by Various Types of Coatings to Aluminum Alloys Buried 4½ to 11½ Years at New Kensington, Pennsylvania

Alloy[1]	Surface Preparation	Protective Coating	Period of Exposure Years[2]	Well-Drained Location		Poorly—Drained (Wet) Location	
				Maximum Pit Depth, Mils	Visual Examination[4]	Maximum Pit Depth, Mils	Visual Examination[4]
1100-H18	None	None	11½	....	a, d	...	b, f
1100-H18	Alrok No. 13	$ZnCrO_4$ + aluminum paint[3]	11½	....	a, i	....	a, i
1100-H18	Phosphoric acid	$ZnCrO_4$ + aluminum paint[3]	7	....	a, k*	....	a, k
3003-H18	None	None	11½	....	b, d	....	b, d
3003-H18	None	Alumilite 202	11½	....	b, d	....	b, e
3003-H18	Alrok No. 13	$ZnCrO_4$ + aluminum paint[3]	11½	....	a, i	....	a, i
6053-T6	None	None	4½	0.7	b	15.0	b, f
6053-T6	None	Alrok No. 13	4½	0.6	b	0.6	b
6053-T6	None	Alumilite 204	4½	0.3	b	0.2	b
6053-T6	Alrok No. 13	2 Coats aluminum paint[3]	4½	....	a, i	....	a, j
6053-T6	Phosphoric acid	2 Coats aluminum paint[3]	4½	....	a, i	....	a, j
6053-T6	Alrok No. 13	1 Heavy coat hot bituminous	4½	....	a, h	....	a, h
2017-T3	None	None	11½	Perforated	d, g	....	g
2017-T3	Alrok No. 13	$ZnCrO_4$ + aluminum paint[3]	11½	....	a, j	....	a, j
43 (Cast)	None	None	11½	....	b, f	....	g
43 (Cast)	Alrok No. 13	$ZnCrO_4$ + aluminum paint[3]	11½	....	a, j	....	a, j
43 (Cast)	Steel grit blast	Metallized with 99.8 percent Al	11½	....	a	....	b, c
112 (Cast)	Steel grit blast	Metallized with 99.8 percent Al	11½	....	a	....	b, c

[1] All wrought materials were exposed as sheet panels 0.064 inch thick; cast materials as panels 0.25 inch thick.
[2] In the case of panels buried 11½ years, all were buried for the first four years at the well-drained site. Then the panels were divided into two groups, one of which was moved to the new, poorly drained location located less than 100 ft. from the other side and close to a small stream.
[3] Phenolic resin varnish vehicle.
[4] Code for visual examination:

Condition of Metal
a — No appreciable attack
b — Etching or superficial pitting
c — Local areas of shallow attack
d — Local incipient exfoliation
e — Many small pits
f — A few relatively deep pits
g — Severe pitting

Condition of Paint Coating
h — Intact, soft and tacky
i — Good, tiny blisters
j — Fair, moderate blistering
k — Poor, many large blisters

* At 4½ years the rating of this panel was a, i.

Figure 8—Shows the excellent condition of the most corroded of nine samples removed from an unprotected 5 mile 6-inch pipe line of welded 6063-T6 in service 7½ years in Arkansas. Arrows indicate small pits, the deepest of these being just 41 mils. The maximum penetration observed on any of the samples was 42 mils on sample No. 7.

TABLE 8—Examination of Samples from Welded 6063-T6 Pipe Line After 7½ Years' Burial in Arkansas

Sample Number	Soil Condition	Visual Appearance[1]	Maximum Pit Depth, Mils[2]
1.....	Sandy, well drained	Very good; some discoloration	.....
2.....	Sandy loam	Very mild attack	.....
3.....	Sandy salt flat	Very good; virtually unaffected	.....
4.....	Sandy loam	Very good; some discoloration	.....
5.....	Sandy, salt water drainage area	Very good; virtually unaffected	.....
6.....	Sandy with high organic content, saturated	Minor pitting	20, 20
7.....	Sandy, well drained	Minor pitting	42, 28
8.....	Sandy loam, saturated	Very good; virtually unaffected	.....
9.....	Sandy, saturated	Few scattered pits	22, 40, 37, 41

[1] Exterior surface of pipe.
[2] Two or more of the deepest pits present were selected for sectioning and microscopic measurement of depth of attack.

oil gathering line near Magnolia, Arkansas. It was buried completely unprotected. After almost eight years of service, nine samples were cut from the line, representing exposure in different types of soils, and submitted for laboratory examination. Table 8 describes the condition of each of these samples and the soil in which they were buried, and Figure 8 is a photograph of sample No. 9 showing the typical discoloration and minor pitting which were encountered. It will be noted in Table 8 that the maximum depth of attack measured was 42 mils. This depth is only 15 percent of the total wall thickness (0.280 inch); even if linear extrapolation is assumed, perforation would not be expected before a total of 53 years. It was noteworthy also that there was no selective attack of the 4043 alloy weld beads or of the adjacent heat-affected zones in the pipe.

In 1956 a buried aluminum pipe line was installed as part of the gas gathering network for Alcoa's Point Comfort, Texas, smelter. This pipe line is 8 inch Schedule 40 alloy 6063-T6 pipe and is about 20,000 feet long. No external coating or wrapping was applied, but standard magnesium anodes were installed on insulated sections to evaluate cathodic protection. The type of soil ranges from sandy loam to dense clay. Figures 9 and 10 are photographs of this pipe line after 3½ years' exposure. The pipe in Figure 9 was unprotected and was immediately adjacent to the cathodically protected pipe shown in Figure 10, the two being separated by an insulating flange. The corrosion of the pipe in Figure 9 was superficial, and there was no corrosion whatsoever on the cathodically protected section shown in Figure 10. A longer exposure will be required to determine whether cathodic protection will be needed in this location.

Coal Mine Service

Recently an inspection was made of a mile of 4 inch Schedule 40 alloy 6063-T6 pipe that had been buried unprotected in a West Virginia underground coal mine for fifteen years. A section of the pipe displaying the most severe external corrosion was examined microscopically. The maximum depth of attack was found to be 120 mils or 50 percent of the total wall thickness (0.237 inch). However, many of the areas of corrosion appeared to be inactive. The pipe line should provide many more years of service.

Stray-Current Corrosion

"Stray-current electrolysis" is a term applied to accelerated corrosion of underground metallic structures caused by stray electric currents originating from external sources. At the initiation of the National Bureau of Standards program of soil corrosion investigations in 1910, it was thought that the presence of stray currents, for example, from the grounding of electrical equipment or leakage from electric railway tracks and power lines was the principal cause of corrosion of underground structures. Corrosion occurs at the point where positive electric current goes from the metal structure to the soil. It was soon learned that serious corrosion of metals in contact with soils also occurred in the absence of stray currents. Nevertheless, stray-current corrosion is a potential problem whenever a metal structure is in contact with soil in the vicinity of large electrical equipment or feeder cables also in contact with the soil.

In the case of an aluminum alloy structure, it is possible to have stray current corrosion not only at the location where the positive electric current goes from the metal to the soil but, also, at a location where the negative current (electrons) is picked up by the soil. Although stray-current electrolysis is generally associated with d-c electricty, corrosion by a-c stray currents is also possible under some conditions.[1,6]

A few cases of severe external corrosion of aluminum pipe in coal mines have occurred as the result of stray direct current effects. A typical coal mine is very hazardous because of the high currents required for operating mining equipment and the fact that electric railway tracks are often used for a return circuit. Also, many locations in coal mines are continuously wet—this condition resulting in areas where the soil has very low resistivity. The reported failures have been in both buried and surface lines strung alongside electric railways and coupled with some type of a quick-acting coupler. Current was evidently picked up either through a direct ground from the rail or return cable or from a zone of soil with very low resistance, and discharged at a location where the resistance through the circuit created by the pipe line was greater than that of the soil.

The quick-acting pipe couplers were not designed to make a good electrical connection, and in some cases they completely insulated the joint. The fact that these couplers created such high resistance was felt to be the major factor contributing to the coal mine failures described. If the electrical resistance of the pipe line is kept low, the general practice of bonding the line to the rails at intervals should prevent the current from going from the line to the ground and prevent the attendant corrosion at those sites. The means for increasing the conductivity of a quick-coupled joint depends upon the design of the coupler. Many coupler manufacturers are considering means of modifying their designs to relieve this problem. Pipe lines with threaded joints or those joined by welding should be good uniform conductors.

Galvanic Corrosion

It is commonly known that when a couple consisting of two or more dissimilar metals or alloys is exposed to an electrolyte the more anodic material will corrode and will electrochemically protect the cathodic material. A galvanic cell is thus set up and the polarity of the cell is dependent upon the solution potentials of the metals in the particular electrolyte. It is frequently stated that a metal will be protected galvanically by any metal above it in the standard electromotive series and will protect any metal below it, but this notion is an oversimplification. Although there is some tendency for the potentials of metals

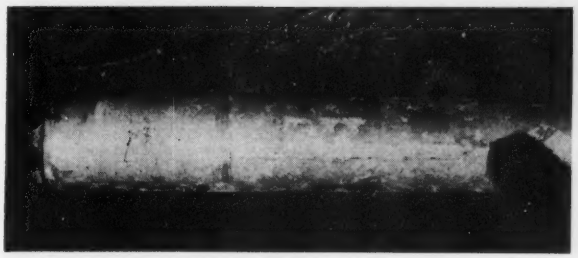

Figure 9—Shows an unprotected section of the 8 inch 6063-T6 alloy gas gathering line at the Alcoa Point Comfort, Texas, Works after 3½ years' exposure underground. Only scattered areas of superficial etching and shallow pitting were observed.

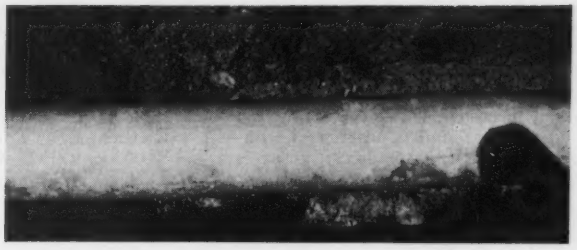

Figure 10—Shown in this photograph is a view taken immediately adjacent to the section of the pipe line shown in Figure 9. The section shown here was cathodically protected by a magnesium anode and was separated from the section in Figure 9 by an insulated coupling. No sign of appreciable corrosion could be seen on this area.

TABLE 9—Potentials of Pipe Specimens Buried at New Kensington, Pennsylvania

Date	6 Inch Diameter Pipe			1¼ Inch Diameter Pipe				
	Months Exposure	Alclad 6063-T6	6063-T6	Months Exposure	6061-T6	Galvanized Steel	Steel	Copper
August 25, 1950	0	—0.762 V.	—0.825 V.	0	—0.571 V.	—1.020 V.	—0.579 V.	—0.069 V.
September 27, 1950	1	0.713	0.734	1	0.719	1.064	0.706	—0.055
October 23, 1950	2	0.690	0.690	2	0.880	1.107	0.744	—0.063
January 5, 1951	4½	0.789	0.832	4½	0.872	1.099	0.737	—0.066
May 18, 1951	9	0.870	0.787	9	0.840	1.110	0.754	—0.074
August 28, 1951	12	0.631	0.545	12	0.414	0.718	0.517	+0.001
March 27, 1952	19	0.753	0.731	19	0.786	1.081	0.761	—0.050
September 10, 1952	24½	0.678	0.601	24½	0.435	0.650	0.529	+0.004
October 7, 1954	49½	0.721	0.682	48½*	0.800	0.876	0.548	—0.020
October 14, 1958	87*	0.621	0.600	86*	0.560	0.610	0.460	+0.010
Range	87*	0.870–0.621	0.832–0.545	86*	0.880–0.414	1.110–0.610	0.761–0.460	—0.074–+0.010
Average	87*	0.723	0.703	86*	0.688	0.934	0.634	—0.041

[1] Potentials referred to a copper-copper sulfate electrode.
[2] Values given are the averages of two or more duplicate specimens.

* Discontinuous periods: 48½ mo = 26½ mo + 22 mo.
86 mo = 26½ mo + 22 mo + 37½ mo.
87 mo = 49½ mo + 37½ mo.

in a particular electrolyte to be arranged in accordance with the electromotive series, the relationship of many couples will reverse when transferred from one electrolyte to another. The extent of galvanic corrosion is dependent upon the potential difference, ratio of anode-cathode areas, polarization characteristics, and resistivity of the electrolyte.

Aluminum alloys have a sufficiently anodic potential in most aqueous solutions that it is reasonable to assume aluminum would be anodic in moist soil to common metals such as steel, brass, and copper. Also, in the majority of cases aluminum alloys will be cathodic to galvanized steel so long as the zinc coating remains intact. Direct contact with galvanized steel may be satisfactory, but it must be expected that the zinc coating on the steel will sacrifice more rapidly than normally in the area adjacent to the couple. Thus, when the zinc is sufficiently consumed, galvanic corrosion of the aluminum can proceed. Anode-cathode area relationships are important in a galvanic cell; since aluminum is normally anodic to other buried metallic structures, it is important that a small area of aluminum not be connected to a large area of cathodic metals.

When the buried pipe specimens were under exposure at New Kensington, Pennsylvania, periodic potential measurements were made. Table 9 lists these values at various dates for aluminum alloys 6061-T6, 6063-T6 and Alclad 6063-T6, galvanized steel, mild steel, and copper. This comparison represents only one soil, but it will be noticed that the general relationships mentioned above prevail.

The common methods of combating galvanic corrosion involve either electrical insulation of the dissimilar metals or cathodic protection. In lapped or flanged connections, insulation can be accomplished with non-conductive gasketing, bushings, and washers; kits containing such items are available for pipe joints. However, satisfactory electrical insulation is not always practicable. If the connection is unavoidable, cathodic protection may be employed to minimize the galvanic attack. For example, anodes of magnesium, or zinc or of aluminum-5 percent zinc alloy could be installed to polarize the cathodic metal structure to the potential of the aluminum structure. In the use of magnesium anodes, the system should be designed to avoid polarizing the aluminum to an excessively electronegative potential because of the danger of creating an alkaline condition at the cathode that can cause corrosion of the aluminum. Present information indicates that the potential should not be more negative than —1.2 V to the copper-copper sulfate reference electrode.

Although paint coatings will provide substantial protection to aluminum alloys in contact with the soil, such coatings are not recommended for aluminum alloy parts to be connected to a structure of a cathodic metal. Galvanic corrosion damage to the aluminum structure would tend to be localized at holidays in the coating and pitting would proceed at a faster rate than if the structure were not coated. Application of the coating to the cathodic structure where this is practicable would be beneficial and may be sufficient.

Conclusions

Service experience with unprotected aluminum alloys in contact with soils, principally in pipe line applications, has generally been favorable except in unusual circumstances involving factors such as stray currents and chemical contaminants. The available field test data, however, show that certain soils may cause severe pitting of aluminum alloys. Also it is very difficult to predict performance on the basis of a chemical analysis or a resistivity measurement of the soil.

Alclad aluminum alloys have demonstrated an outstanding resistance to penetration by pitting in comparison to other aluminum alloys. Other wrought and cast aluminum alloys, with the exception of those containing copper as one of the major alloying additions, have shown a somewhat similar resistance to soil corrosion and were generally superior to mild steel. The generally less corrosion resistant copper-bearing alloys have exhibted a resistance to soil corrosion similar to that of steel.

Conventional coating materials and coating and wrapping procedures used on mild steel are normally quite suitable for aluminum alloys. It has been demonstrated that cathodic protection of underground aluminum structures is feasible and may eventually permit bare aluminum alloys to be buried in even the most corrosive coils. It appears that lower current densities are required to cathodi-

cally protect aluminum than steel; in fact, excessive currents can cause cathodic corrosion and must be avoided.

The test data and service experience now available indicate that aluminum alloy products should be considered for use underground or in contact with soil. In most cases, it should not be necessary to protect alclad products. However, protection should be considered for non-clad products except in temporary installations or in locations where previous experience with aluminum has demonstrated its suitability.

Acknowledgments

Many of the investigations included in this paper were originated by R. H. Brown, Assistant Director of Research, and R. I. Wray, Chief of the Paint Finishes Section of the Finishes Division of Alcoa Research Laboratories, in cooperation with E. T. Wanderer, Manager of the Petroleum Section of the Alcoa Sales Development Division. Acknowledgment is made of their suggestions as well as those of C. J. Walton, Chief of Finishes Division; E. T. Englehart, Assistant Chief of Chemical Metallurgy Division, and D. G. Vandenburgh, Research Engineer in Chemical Metallurgy Division of Alcoa Research Laboratories.

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Any discussion of this article not published above will appear in June, 1961 issue.

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Chloride Corrosion and Fouling In Catalytic Reformers With Naphtha Pretreaters*

By E. B. BACKENSTO* and A. N. YURICK*

Abstract

A study was made of chloride corrosion and fouling occurring in low-temperature sections of catalytic reformer naphtha pretreaters. These problems were related to corrosion by aqueous HCl-H_2S-NH_3 solutions. Laboratory corrosion studies were made with these solutions to establish the effect of pH and composition in the presence or absence of an air atmosphere. Suppression of corrosion by ammonia neutralization and amine-type inhibitors also was studied.

Elevated temperature tests were conducted in a nitrogen atmosphere. Field tests were made on six metals in a commercial pretreater reactor effluent stream. The removal of ammonium chloride fouling deposits was discussed briefly.

8.4.3, 4.3.2, 5.7.7, 3.3.2

Introduction

THE RAPID growth of catalytic reforming, as a means for upgrading motor and aviation gasoline, has been accompanied by a number of corrosion problems. Initially, the most serious problem was one of high-temperature hydrogen sulfide corrosion. The first paper dealing with this problem was given in 1955.[1] Reports by others followed, including high-temperature catalytic reformer corrosion data compiled and correlated as a contribution to the work of NACE Technical Group Committee T-8.[2]

One way found effective for controlling this high-temperature corrosion was to desulfurize the naphtha charged to the catalytic reformer. Pretreating naphthas catalytically in a hydrogen atmosphere is now a general practice in most catalytic reformers, for corrosion as well as process considerations.

Today, high-temperature hydrogen sulfide corrosion is under control. But other problems have been encountered, largely in pretreating sections of reforming units. Corrosion and fouling by chlorides in low-temperature sections of the pretreater is one of the most serious problems encountered.[3] While control methods are being used commercially, very little information on this corrosion and fouling problem appears in the literature. This paper will summarize laboratory studies simulating chloride corrosion and fouling in naphtha pretreaters.

Corrodents Formed in Pretreater

In pretreating the naphtha most of the compounds that contain sulfur, oxygen, nitrogen, or chlorine are destroyed in the hydrogen atmosphere. The by-products of this destruction are H_2S, H_2O, NH_3, and HCl. Under certain conditions, these gases are corrosive or combine to form inorganic fouling deposits. The corrosion and fouling occurs after the pretreater reactor as the naphtha stream is cooled in a series of exchangers. The deposition generally occurs below 400 F.

Organic chlorine compounds in the naphtha may be blamed for most of the troubles. The HCl formed in the pretreater may concentrate at moist low-temperature locations and cause severe acid attack, or HCl may combine with NH_3 to produce ammonium chloride fouling deposits. In such systems containing H_2S, corrosion is often accelerated under these fouling deposits.

Ammonium chloride fouling deposits plug exchanger tubes, thus reducing heat transfer rate and increasing pressure drop. Intermittent on-stream water flushing is generally practiced to rid the system of these deposits. In some units water as a diluent and ammonia as a neutralizer have been injected continuously at a low rate to prevent corrosion in low-temperature sections of pretreaters. Amine-type inhibitors are also added for corrosion control, depending upon the corrosion severity of the system. In other units a combination of continuous and intermittent flushing is practiced.

Laboratory Tests

Laboratory tests were conducted to obtain a better understanding of what happens in commercial units when water is injected into heat exchangers containing inorganic fouling deposits. The aqueous HCl-H_2S-NH_3 system was selected as simulating field conditions. Laboratory tests were based on solutions containing a total of 500 ppm of these three components. The relationship at room temperature between pH and composition for the aqueous HCl-H_2S-NH_3 system is shown in Figure 1. The iso-pH lines at a constant pH of 3, 6, and 8 are shown. The slopes of these lines indicate that H_2S has only a slight influence on the pH of these solutions.

Bench scale corrosion tests were conducted using solutions of this aqueous system. The test solutions were placed in a glass bottle containing carbon steel coupons suspended from glass hooks. The test solution was purged with nitrogen in an attempt to exclude air. The test assembly was placed in a horizontal shaker and agitated for 24 hours at room temperature and atmospheric pressure. Corrosion rates were calculated from the weight loss of the coupons.

Figure 2 summarizes results obtained by the bench scale corrosion test. It may be seen that the iso-corrosion lines roughly parallel the iso-pH lines shown in Figure 1, with corrosion increasing as the solution becomes more acid.

Figure 3 illustrates similar corrosion test results where the nitrogen purge was eliminated and air occupied the space above the test solution. By comparison with Figure 2, it can be seen that the presence of air substantially increased the corrosiveness of the solution. Actually, solutions exhibiting essentially no corrosion in a nitrogen atmosphere gave 20-30 mils per year corrosion in the presence of air. These data also show, by comparison along the HCl-NH_3 composition line (no H_2S present), that addition of NH_3 with the flushing water to raise the pH of the system will be less effective for reducing corrosion when air is present. The curves at both ends of the iso-corrosion lines in Figure 3 are probably the result of losing NH_3 and H_2S during the test.

The effectiveness of both oil-soluble and water-soluble amine-type inhibitors were also tested by this bench scale corrosion test. In a nitrogen atmosphere, most of the inhibitors tested significantly reduced the corrosiveness of the HCl-H_2S-NH_3 system solutions. For example, the addition of 50 ppm of inhibitor in one of the most corrosive solutions (500 ppm HCl) reduced corrosion to less than 2 mpy. However, in an air atmosphere none of the inhibitors was very effective. As a matter of fact, in solutions containing no H_2S the addition of inhibitor actually increased corrosion of the carbon steel coupons.

Ammonia Neutralization

One of the more corrosive solutions (400 ppm HCl-50 ppm H_2S-50 ppm NH_3, pH = 2.3) was selected to study the effect of neutralization with NH_3. As NH_3 is added to this solution the resulting neutralization curve is typical of a titration curve of a strong acid with a weak base. The first few increments of added NH_3 have very little effect on the pH of the solution. At the neutralization point the pH changes very rapidly. After this point is reached, increments of added NH_3 have very little effect on pH.

The effect of NH_3 neutralization on corrosion determined by the bench scale test is shown in Figure 4. In a nitrogen atmosphere, corrosion was reduced more than 95 percent whereas in an air atmosphere corrosion was reduced only about 35 percent. The maximum benefit was not attained until sufficient NH_3 had been added to increase the pH above 8.

In a nitrogen atmosphere, hydrogen blisters were evident on the test coupons below 8 pH; at the higher pH levels

★Submitted for publication August 4, 1960. A paper presented at a meeting of the Northeast Region, National Association of Corrosion Engineers, Huntington, West Virginia, October 11-14, 1960.

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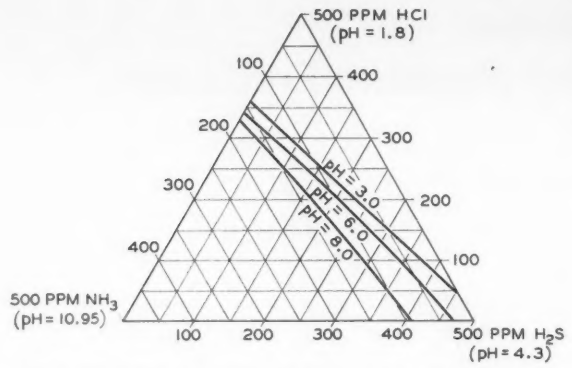

Figure 1—Iso-pH lines for the aqueous HCl-H_2S-NH_3 system (500 ppm total).

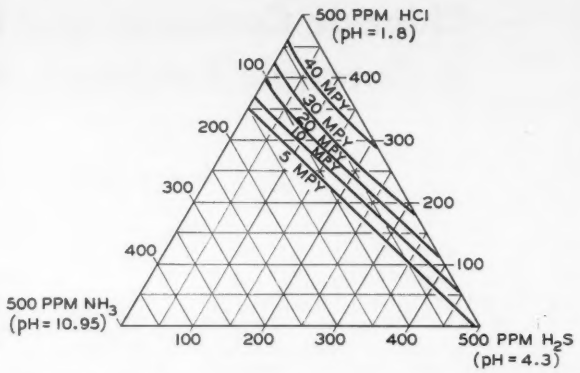

Figure 2—Iso-corrosion lines for carbon steel in aqueous HCl-H_2S-NH_3 system (500 ppm total; nitrogen atmosphere, room temperature and atmospheric pressure).

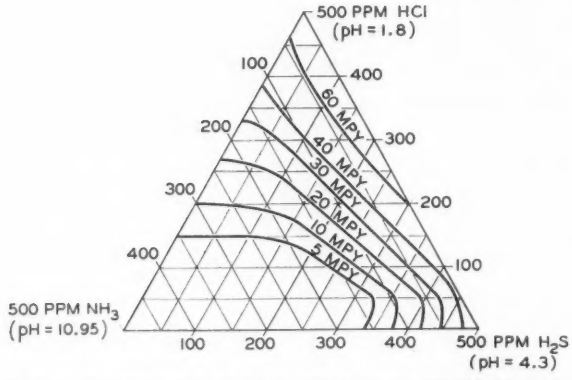

Figure 3—Iso-corrosion lines for carbon steel in aqueous HCl-H_2S-NH_3 system (500 ppm total; air atmosphere, room temperature and atmospheric pressure).

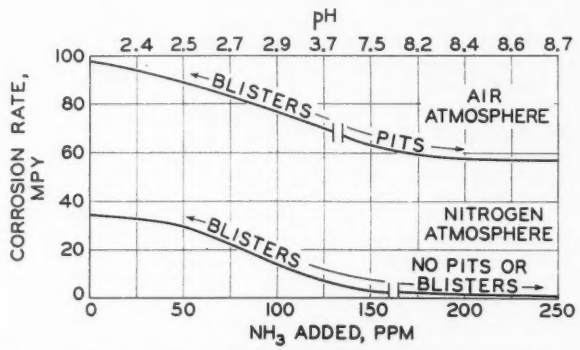

Figure 4—Effect of HN_3 neutralization on corrosion of carbon steel in an aqueous solution containing 400 ppm HCl, 50 ppm H_2S, 50 ppm NH_3 at room temperature and atmospheric pressure.

there was no evidence of pits or blisters. In an air atmosphere, hydrogen blisters were evident on the test coupons below the neutralization point; above the neutralization point pitting was evident as the result of anodic attack.

These findings emphasize the importance of avoiding air being drawn into any flushing stream used in pretreater heat exchangers. Although oxygen would not normally be present at this point of a commercial system, air could be drawn in, for example through a leaking packing gland on the pump used for flushing solution. Test data obtained at room temperature and atmospheric pressure show the following harmful effects of oxygen:

1. Corrosion is increased about threefold.
2. Neutralization with NH_3 is only one-third as effective.
3. Inhibitors lose their effectiveness and may actually accelerate corrosion.

Elevated Temperature Tests

To more nearly simulate commercial NH_3 neutralization conditions, rocker bomb tests were conducted at 300 F and 625 psig in a nitrogen atmosphere for 24 hours. In these tests, carbon steel coupons suspended from glass hooks were immersed in the test solution contained in a glass bomb liner. Again, an aqueous solution containing 400 ppm HCl, 50 ppm H_2S, and 50 ppm NH_3 was selected for this work. The pH measurements reported for elevated temperature tests were made at room temperature.

In these elevated temperature tests two general types of corrosion attack were noted. Typical examples of both types of corrosion are shown in Figure 5. Most of the time, the corrosion product was a loose deposit, easily removed by scrubbing with soap and water. Other times part of the corrosion product was a tight, black film that could not be removed by the conventional cleaning procedure. The loose deposit was mainly kansite, Fe_9S_8, while the nonremovable film was mainly magnetite, Fe_3O_4. Usually there was some loose deposit over the tight, black film. Actually, higher corrosion rates were found with coupons having a non-removable magnetite film. There is no apparent explanation to account for these different types of corrosion. It appears, however, that some air may have been present to help form the oxide film even though care was taken to exclude air in all high temperature tests.

Figure 6 shows the effect of NH_3 addition on corrosion in tests where only loose sulfide corrosion products formed. It can be seen that corrosion decreases with NH_3 addition, but tends to remain constant above 8.2 pH. However, even at high pH levels the addition of NH_3 only decreased corrosion about 50 percent. All coupons exposed to low pH solutions showed hydrogen blisters. Coupons showed no pits or blisters when exposed to solutions of 7.5 pH or higher.

Figure 7 shows the effect of NH_3 addi-

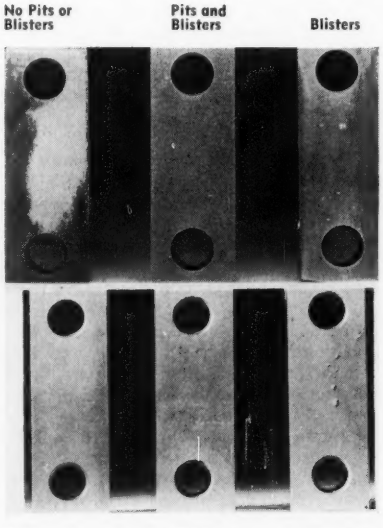

Figure 5—Types of corrosion attack noted on carbon steel in aqueous HCl-H_2S-NH_3 solutions at 300 F and 625 psig under nitrogen. On top three specimens note tight black, film (approximately full size); on bottom specimens note absence of tight, black film.

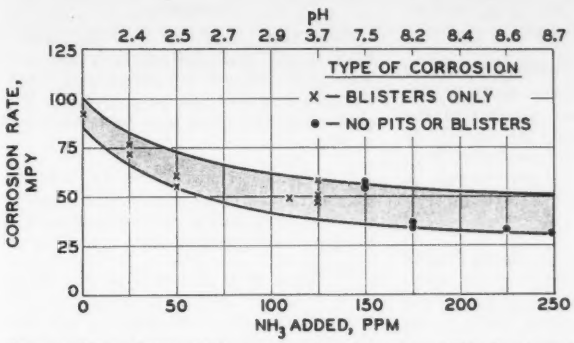

Figure 6—Effect of NH_3 addition on corrosion when only a sulfide film formed on the test coupons. Carbon steel coupons were in aqueous HCl-H_2S-NH_3 solutions for 24 hours at 300 F and 625 psig under nitrogen.

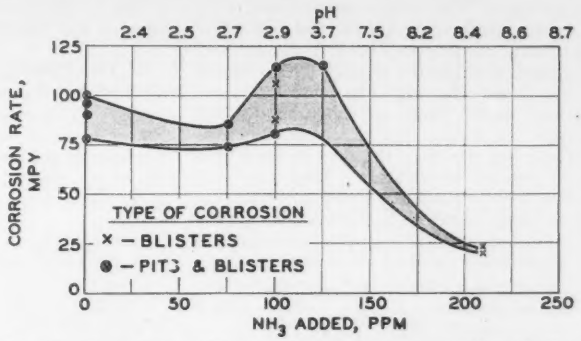

Figure 7—Effect of NH_3 addition on corrosion when non-removable oxide film formed on the test coupons. Carbon steel coupons were in aqueous HCl-H_2S-NH_3 solutions for 24 hours at 300 F and 625 psig under nitrogen.

TABLE 1—Corrosion Test Results Obtained in a Commercial Pretreater Reactor Effluent Stream

	RACK NO.			
	S-1	S-2	S-3	S-4
Est. Conditions:				
Temperature, F	465	415	310	205
Pressure, psig	460	455	450	425
Exposure Time, Days	190	190	190	190
Materials Tested:	Corrosion Rate, MPY			
Carbon Steel, ASTM A-7	5.0	1.6	46.0	1.9
18-8S, Type 304	0.2	0.1	0.3	<0.1
18-8 SL, Type 304L	0.2	0.2	0.2	0.1
Incoloy	<0.1	<0.1	<0.1	<0.1
Inconel	0.2	0.1	0.6	<0.1
Monel	5.1	0.9	3.1	4.9

tion on corrosion in tests where a magnetite film remained after the conventional cleaning procedure. The data show that after the first incremental additions of NH_3 corrosion is decreased only slightly. As more NH_3 is added to neutralize the solution corrosion increases and may actually be higher than without NH_3 addition. Above the neutralization point, as the pH is raised to about 8.5, corrosion decreases rapidly. All the coupons showed hydrogen blisters after the test; most of the coupons tested at low pH also were pitted.

Water flushing to free exchangers of ammonium chloride fouling deposits produces a corrosive, low pH solution. Tests at elevated temperature illustrated that corrosion by such a solution is more complex than would be predicted from room temperature results. Actually, corrosion cannot be eliminated at elevated temperature by simple neutralization. Therefore, when NH_3 is added to the water flush, laboratory data indicate the following:

1. The maximum reduction of corrosion by neutralization with NH_3 is not obtained until the pH is increased to at least 8.2.

2. Neutralization with NH_3 to an intermediate pH (3-6) may actually result in higher corrosion rates than those obtained without adding NH_3.

Inhibitor Tests

Amine-type inhibitors also were tested for their effectiveness at elevated temperature. The same test as described for the neutralization studies was used: 300 F, 625 psig, nitrogen atmosphere, test solution 400 ppm HCl-50 ppm H_2S-50 ppm NH_3. Inhibitor concentration was 50-100 ppm. The test results may be summarized as follows:

1. None of the inhibitors tested was very effective for reducing corrosion unless the solution was partially neutralized with NH_3.

2. Without NH_3 neutralization, inhibitors reduced corrosion only by 30-40 percent. Very few inhibitors prevented blistering and pitting of the test coupons.

3. In a neutralized solution (pH = 8.0), most of the inhibitors tested reduced corrosion to below 15 mpy. However, not all of the inhibitors eliminated pitting of the test coupons.

4. Several of the inhibitors were just as effective in a partially neutralized solution (pH = 3.6-5.6) as in a completely neutralized solution.

Field Tests

In several commercial units, corrosion has been severe in pretreater reactor effluent exchanger tubes. To evaluate corrosion severity, test racks were placed in commercial units. The test racks were constructed of Monel; the coupons were isolated from the rack with polytetrafluoroethylene washers as shown in Figure 8. The test racks were tack welded to exchanger heads and were exposed to the pretreater reactor effluent stream. Typical results are summarized in Table 1. Although tube failures occurred as a result of corrosion during the test period, corrosion measured by the test coupons

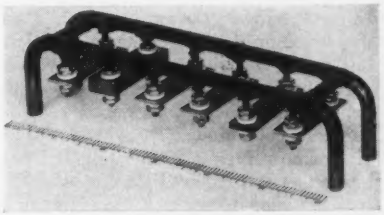

Figure 8—Low-temperature corrosion test rack.

was relatively low, generally 2-5 mpy on carbon steel. Of course, the location of these racks was such that fouling deposits did not accumulate on the test coupons. Fouling deposits, however, did accumulate in the exchanger tubes to cause increased pressure drop across the exchanger train.

From test rack field data it was concluded that the pretreater effluent stream is not very corrosive in itself under the conditions of temperature prevailing in the exchanger train. Therefore, it appears the severe corrosion observed on exchanger tubes in commercial units is the result of corrosion under deposits.

After the exchangers are flushed with water, FeS is found to be the main component of the exchanger deposit. The FeS found in the hotter exchangers, operating above 400-500 F, is probably the result of high-temperature H_2S corrosion. In exchangers operated below 400 F, the FeS is thought to be formed by the following reaction:

$$2NH_4Cl \xrightarrow{H_2O} 2HCl + 2NH_3$$

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

$$FeCl_2 + (NH_4)_2S \rightarrow FeS + 2NH_4Cl$$

The $FeCl_2$ is the product of acid-type corrosion under moist NH_4Cl deposits. Ammonium sulfide or hydrosulfide, which are relatively unstable, are also expected to be present as part of the original water soluble deposit. It should be noted that when FeS forms, the original amount of ammonium chloride is still present as part of the deposit.

Laboratory tests were designed to evaluate corrosion under fouling deposits. A 3-inch length of ¾-inch, 16 gauge, carbon steel tubing was selected as the test

specimen. The tube was packed with equal weights of NH_4Cl and FeS. For 10 days 1.5 percent H_2S in hydrogen was passed through the deposit-filled tube at 350 F and 465 psig. The corrosion measured on the inside of the tube was 0.2 mpy. A similar test was run for four days, but this time the deposit contained 15 percent wt moisture, After this test, the average corrosion inside the tube was 37 mpy; visual inspection showed that corrosion on the bottom of the tube was considerably greater than the average. These tests demonstrated that the severe corrosion of exchanger tubes occurs under moist fouling deposits.

Removal of Fouling Deposits

Ammonium chloride fouling deposits in commercial pretreater exchangers have been removed successfully by on-stream water flushing. The water is separated from the product stream in a flash drum down-stream of the exchangers. Continuous water injection may aggravate the corrosion problem by keeping the NH_4Cl deposits moist. Therefore, deposits should be removed periodically by water slugging. The principle of slugging is based on getting the required amount of water into the system for the shortest practical time. The following points are important:

1. Enough water must be injected to saturate the effluent stream at the temperature and pressure prevailing and to dissolve the NH_4Cl present.

2. The frequency of slugging will be dictated by the pressure drop or the amount of nitrogen and chlorine in the charge naphtha. Normally the amount of nitrogen in the stock will be controlling; however, when the nitrogen content is high, the chlorine content will be controlling.

3. Corrosion will be accelerated only during the short periodic slugging operation since severe corrosion of exchanger tubes is the result of attack under moist NH_4Cl deposits. Under normal dry conditions, the corrosivity of the stream should be very low.

4. If infrequent slugging is required, no corrosion control may be needed. If slugging is required more than once a week, neutralization may be indicated. In extreme cases, inhibitor addition also may be required. The amount of neutralizer should be controlled to maintain an 8.0-8.5 pH of the water drawn off at the separator.

5. Efforts must be made to avoid corrosion under deposits, for water insoluble FeS is the resultant corrosion product. Water slugging is not effective for removal of FeS and the FeS will accumulate in the system to add to the plugging and pressure drop problem.

Summary

Laboratory tests and field experiences have shown that chloride corrosion and fouling in catalytic reformers with naphtha pretreaters can be controlled. The major considerations may be summarized as follows:

1. The pretreater reactor effluent stream should be kept as dry as possible, for severe corrosion occurs under moist inorganic fouling deposits.

2. When it is impractical to operate with a dry pretreater effluent stream, neutralization with inhibition is the most effective means for controlling corrosion.

3. Pressure drop caused by inorganic fouling deposits can be relieved by short periodic on-stream water slugging. For slugging to be effective, the process stream must be saturated with water.

4. Corrosion is accelerated in the presence of air; therefore, air should not be introduced with injection streams.

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2. G. Sorell. Compilation and Correlation of High Temperature Catalytic Reformer Corrosion Data. *Corrosion*, **14**, No. 1, 15t-26t (1958) Jan.
3. E. B. Backensto and R. W. Manuel. Corrosion Experience in Catalytic Reformers with Naphtha Pretreaters. *Proc. API*, 38 (III), 31-37 (1958); condensed article, *Oil & Gas J*, **56**, No. 20, 131-5 (1958).

Any discussion of this article not published above will appear in June, 1961 issue.

Kinetics and Mechanism of Hydrogen Attack of Steel*

By L. C. WEINER*

Abstract

The kinetics of hydrogen attack of a killed steel have been studied in the temperature range 800 to 1200 F and in the pressure range 450 to 950 psi hydrogen. A quantitative relationship between incubation of attack and temperature and pressure has been obtained. Based on these results and those from a series of iron alloys, a model is presented in which (1) incubation is controlled by the reduction of grain boundary iron oxides forming water vapor which acts to inhibit the accumulation of methane in the boundaries by reacting with it; (2) grain boundary methane pressure forming a network of fissures and/or stress concentrators acts as the embrittling agent; (3) when the carbides are stabilized by spheroidization or alloying, resistance to attack is increased since carbide dissolution controls both incubation and embrittlement. 3.2.2, 6.2.1

Introduction

A NUMBER of petroleum and petrochemical industries processes involve the use of hydrogen under pressure and at elevated temperatures. Steel structures and components, primarily plain carbon steel, subjected to these environmental conditions for sufficient periods of time can be so damaged as to cause service failures when a sufficient load is present. This damage is mainfested as internal decarburization and intergranular fissuring accompanied by reduced ductility and strength properties. This phenomenon known as "hydrogen attack," has been observed in both irons and steels.[1, 2, 3, 4] It is differentiated from the reversible type of hydrogen embrittlement in that ductility cannot be restored by driving out residual hydrogen during a low temperature heat treatment.

While systematic experimentation has been carried out on reversible hydrogen embrittlement, data accumulated on the phenomenon of hydrogen attack have been limited primarily to service experience.[3, 4, 5, 6] Earlier laboratory work also has been reviewed by Schuyten.[6] While experimental work on irons[1, 2] was not associated with that on steels, the behavior recorded was so similar that it can be considered in the same category. The embrittlement of the irons was thought to be due to the fissuring of grain boundaries by pressure build-ups of molecular hydrogen[1] or water vapor as a result of reaction of hydrogen and oxides at the boundaries.[2] With steels, hydrogen attack has generally been thought[6] to be due to the following sequence of events. Hydrogen, either in atomic or protonic form, permeates and diffuses into steel. Hydrogen reacts with iron carbides at the grain boundaries to form methane; this constitutes internal decarburization. Methane pressure builds up to high values and since it is unable to diffuse out of the steel, localized grain boundary fissuring occurs giving rise to deterioration of the material.

Since there were few quantitative data on hydrogen attack available, as well as no experimentally proven model of this phenomenon, this investigation was undertaken to achieve these goals, with the knowledge that a basic comprehensive understanding should lead to means of tolerating and retarding or preventing this type of embrittlement.

Experimental Procedure

A commercial steel and a series of vacuum remelted iron-carbon alloys were studied in this investigation. The chemical analysis of the killed steel and the iron alloys (F series) are given in Table 1. The initial iron used in the F series alloys was a vacuum melted iron, 99.900 percent purity in which oxygen was the largest impurity (by a factor of 10 greater than any other impurity). With the additional alloying components, the iron was remelted in a molecular still vacuum furnace[7] to give this series of alloys having low oxygen content.

Miniature round tensile specimens, 0.5 inch gauge length and 0.09 inch diameter, were carefully machined. The gauge lengths were polished down through 2/0 paper so that the last scratches were parallel to the axis of the specimen. The diameters along the entire gauge length were accurately measured to within ± 0.0001 inch with an optical comparator and a mean value of specimen diameter was obtained. While the F series specimens, machined from hot swaged rods, were heat treated (in a slightly positive pressure of hydrogen to prevent oxidation) to give a fairly uniform ferritic grain size of between ASTM Nos. 5 and 6, the killed steel specimens had a uniform ferritic grain size of ASTM No. 7.5 and needed no further heat treatment. Specimens of this steel having a ferritic grain size of ASTM No. 5 obtained by heat treating at 2000 F (in a slightly positive pressure of hydrogen) were also studied.

Groups of 3 or 4 specimens of the steel, and 2 specimens of the iron alloys, were exposed at the desired temperature and hydrogen pressure for desired lengths of time. The specimens were placed in steel holders so that their total surface areas were exposed, and these in turn inserted in a stainless steel tube in which exposure was carried out. Resistance furnaces controlled to give exposure temperatures to within ± 10 F were used. Chromel - alumel thermocouples peened into the outside wall of the tube were used to measure the temperature which was found to be identical to that of a thermocouple placed within the tube next to the specimens. A static exposure environment of untreated tank hydrogen whose pressure was measured to within ± 10 psi was employed. Subsequent to the exposure, the specimens were baked in a nitrogen atmosphere at 400 F for one hour to remove any residual hydrogen.

Tensile tests were carried out at room temperature in an Instron testing machine at a crosshead speed of 0.5 inch/min. The final diameters of the broken specimens were measured and reduction of area values were calculated. For each

About the Author

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TABLE 1—Chemical Analysis of Steel and Iron Alloys

Element	Percent Content for Steel and Iron Alloys				
	Steel	F-1	F-2	F-3	F-4
Carbon	0.19	0.0042	0.032	0.25	0.29
*Oxygen	0.0050	0.0026	0.0020	0.0029	0.0022
Nitrogen	0.0076	0.0025	0.0025	0.0025	0.0018
Manganese	0.70	.....	.....	.....	.....
Silicon	0.19	.....	.....	.....	.....
Sulfur	0.015	.....	.....	.....	.....
Phosphorous	0.015	.....	.....	.....	.....
Aluminum (Acid Soluble)	0.017	.....	.....	0.11**	<0.001

* Total oxygen content including all oxides.
** 0.1 percent aluminum added as deoxidizer.

★ Submitted for publication July 27, 1960.
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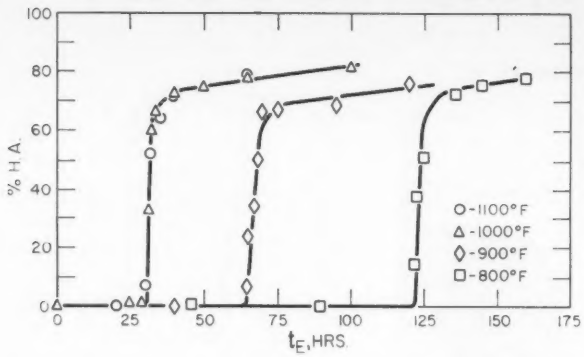


Figure 1—Hydrogen attack of steel as a function of exposure time at 700 psi hydrogen pressure.

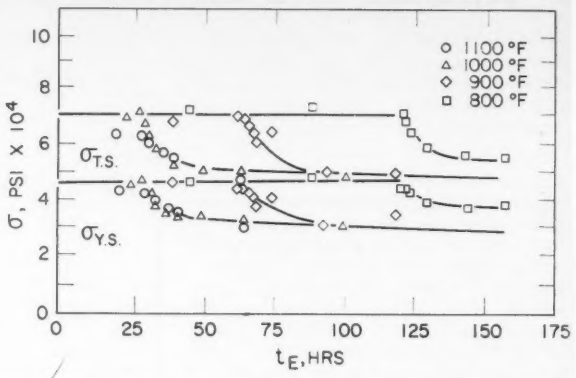
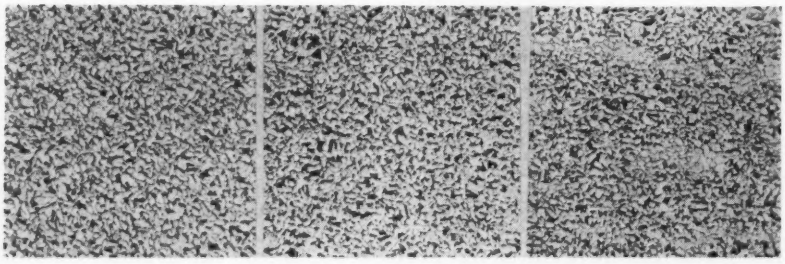
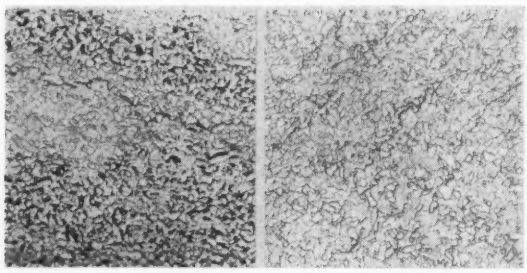


Figure 3—Strength properties of steel as a function of exposure time at 700 psi hydrogen.



A— 0 hours; 0% H.A. B—29 hours; 0% H.A. C—31 hours; 33.1% H.A.



D—40 hours; 72.5% H.A. E—80 hours; 81.5% H.A.

Figure 2—Microstructures of steel specimens exposed for various times at 1000 F and 700 psi hydrogen pressure. $t_o = 30$ hours. Nital etched, approximately 50X.

group of specimens a mean value was obtained. Since hydrogen attack is primarily manifested as reduced ductility properties, hydrogen attack is defined here as the percent loss in reduction of area. Materials can be compared regardless of their original ductility by utilizing this definition.

Experimental Results

Steel

Effect of Exposure Temperature Figure 1 presents plots of percent hydrogen attack versus exposure time at 800, 900, 1000, and 1100 F and at a constant hydrogen exposure pressure of 700 psi. The curves all had the same shape and are displaced along the exposure time axis as exposure temperature, T_E, decreases. The time before which no permanent embrittlement occurs, as indicated by the criterion selected, is called the incubation time, t_o. It is clearly seen that up to 1000 F, the effect of T_E on the kinetics of hydrogen attack is primarily manifested as a pronounced effect on t_o. Once attack is initiated, it rapidly proceeds to an advanced state of deterioration. Increasing exposure temperature causes a decrease in incubation time. While no definite systematic effects of T_E were observed on the attack rates (the curves themselves), there are insufficient data to establish this as a conclusion. In any event, if T_E does have some effect on these rates, it is small over the temperature range studied and minor relative to its effect on t_o.

In all cases of attack, fractures were brittle, entirely intergranular in nature, as compared to the familiar cup and cone type fractures in unattacked material. In addition, hydrogen attack was accompanied by internal decarburization and the formation of both fine fissures and voids at the grain boundaries. Figure 2 shows a series of photomicrographs of specimens exposed for various times at 1000 F in 700 psi hydrogen pressure ($t_o = 30$ hours) which demonstrate these effects as the material becomes progressively more embrittled.

In addition to the deterioration of ductility, strength properties were also affected and as seen in Figure 3, both tensile and yield strengths decrease concomitantly with ductility. The percentage decrease of both strength properties was approximately 33 percent and since internal decarburization occurred, the major portion if not all of this decrease was probably due directly to the loss of carbon from the steel.

From the data observed at 1100 and 1200 F (Figure 4), it became evident that t_o goes through a minimum between 1000 and 1100 F. This suggests that above this minimum another process is coming into play and is acting in an opposite direction to the rate controlling process operating below this temperature. A plot of ln t_o vs. $1/T_E$ (K°) is shown in Figure 4 for an exposure pressure of 700 psi. Although a "C" type curve results, up to 1000 F a straight line relationship holds which can be written as an Arrhenius type of equation as follows:

$$t_o = Ae^{Q/RT_E} = 3.78 \times 10^{-3} e^{14{,}600/RT_E} \quad (P_E = 700 \text{ psi}) \qquad (1)$$

where T_E is exposure temperature in degrees Kelvin, R the gas constant, A the reciprocal of the frequency factor, and Q the apparent activation energy in cal/mol.

Effect of Exposure Pressure. The effect of hydrogen exposure pressure, P_E, on the kinetics of hydrogen attack was investigated at 900 F and at pressures of 450 and 950 psi, in addition to the observations already recorded at 700 psi. Figure 5 gives these results as a plot of percent hydrogen attack vs. exposure time. The curves are essentially the same as were observed previously (Figure 1). Similar to exposure temperature, the effect of P_E is primarily manifested as a pronounced effect on t_o. Increasing exposure pressure decreases incubation time. The attack rates appear little af-

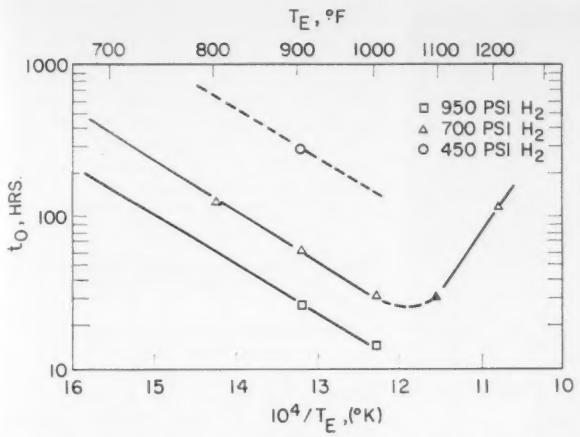


Figure 4—Incubation time as a function of the reciprocal of absolute temperature.

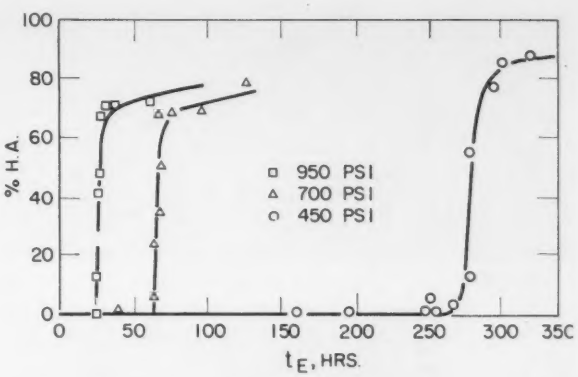


Figure 5—Hydrogen attack of steel as a function of exposure time at 900 F for various hydrogen exposure pressures.

fected by exposure pressure. Analysis of these data results in the following relationship:

$$t_o = B\ P_E^{-n} = 2.28 \times 10^{10}\ P_E^{-3} \quad (T_E = 900\ F) \quad (2)$$

where P_E is exposure pressure in psi, and B and n are constants.

While the relationship between t_o and P_E was observed at only one temperature, it was desirable to know whether or not it held at other exposure temperatures. From Equations (1) and (2) assuming that Q (14,600 cal/mol) is independent of P_E gives the relationship:

$$t_o = C\ P_E^{-n} e^{Q/RT_E} = 1.39 \times 10^6\ P_E^{-3} e^{14,600/RT_E} \quad (T_E \leqq 1000\ F) \quad (3)$$

where C is a constant. From the above equation, a value of 13.2 hours is predicted for t_o at 1000 F and 950 psi hydrogen pressure. Experimentation carried out at these exposure conditions gave a t_o value of 14.5 hours, in excellent agreement with the predicted value, especially when the standard deviation of Equation (3), 9.3 percent, is considered. The additional data at 950 psi in Figure 4 demonstrate that within experimental accuracy, Q is independent of hydrogen exposure pressure thereby substantiating the assumption which was used in formulating Equation (3).

Additivity of Exposure Time. In many instances while studying the effects of T_E and P_E, it was demonstrated that exposure time, t_E, is accumulative regardless of the number and duration of unexposed time intervals; t_E does not revert back to zero upon interruption of the exposure. Also, exposure time at various sets of exposure conditions should be accumulative in a proportional manner to give a total equivalent time of exposure at any one set of conditions. These observations point out the irreversible nature of this phenomenon.

Effect of Spheroidization. The microstructures of specimens exposed at 1200 F and 700 psi hydrogen pressure indicated that some spheroidization had occurred and it was thought that this might be the competitive and opposing process causing an increase in t_o at temperatures above those where the minimum appeared (Figure 4). As a result, a series of specimens were run in which the specimens were pretreated at 1310 F for various times (in a slightly positive pressure of hydrogen to prevent oxidation) in order to give various degrees of spheroidization. These pretreated specimens were then exposed at 900 F and 700 psi hydrogen pressure. The results of these specimens are shown in Figure 6, a plot of t_o vs. pretreatment time at 1310 F, which is in effect a measure of the degree of spheroidization (Figure 7). As is seen from the plot, a straight line relationship exists between t_o and degree of spheroidization in which t_o is increased almost five fold over that value observed with material having a lamellar pearlitic structure.

Effects of Ferrite Grain Size, Specimen Size and Surface Condition. Although these variables were not studied fully, the results are important when considering any model for this phenomenon. At the exposure conditions of 1000 F and 700 psi hydrogen pressure, t_o was found to be 50 hours for material having a ferritic grain size of ASTM No. 5 (measured average apparent grain diameter of 0.00257 inch) as compared to 30 hours for material having a ferritic grain size of ASTM No. 7.5 (measured average apparent grain diameter of 0.00115 inch). Similar to the fine grained material, the microstructure of the larger grained material showed lamellar pearlite of about the same fineness and thus, this increase in t_o can be directly related to the increase in grain diameter.

Although the cross-sectional area in the gauge length of the tensile specimens

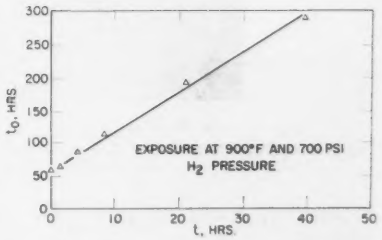
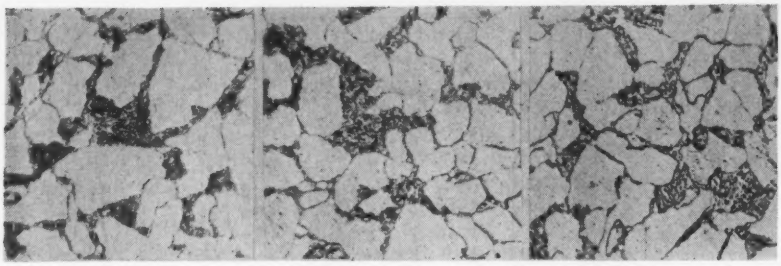


Figure 6—Incubation time as a function of pretreat time at 1310 F prior to exposure at 900 F and 700 psi hydrogen pressure.

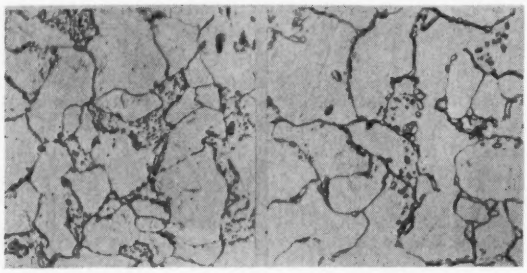
was varied four-fold, no effect of specimen size on hydrogen attack was observed. Similarly, specimens whose surfaces were oxidized prior to exposure behaved in an identical manner to those having clean polished surfaces.

Recovery from Hydrogen Attack. Although hydrogen attack has been considered irreversible in that removal of residual hydrogen does not result in restoration of ductility, experiments carried out at elevated temperatures demonstrated that recovery from attack is possible. Specimens which were exposed for 70 hours at 1000 F and 700 psi hydrogen pressure to give 81.5 percent hydrogen attack (an advanced state) were subsequently heated at temperatures between 1250 and 1650 F in a slightly positive pressure of hydrogen to prevent oxidation.

Figure 8 shows these results as a plot of percent recovery versus recovery temperature. Within experimental accuracy, no further change occurred with recovery treatments longer than one-half hour; the points of the curve represent mean values of recovery. As is seen from the curve, a restoration of ductility as great as 90 percent was obtained at a recovery temperature of 1650 F and perhaps even a larger amount could be restored at higher temperatures. Although recovery of ductility was recorded, restoration of strength properties was not observed. However, while a yield point was not observed with material attacked more than about 20 percent, recovery treatments, even those which resulted in only slight restoration



A—1 hour B—3.5 hours C—7 hours



D—21 hours E—40 hours

Figure 7—Microstructures of steel showing the effect of pretreatment time at 1310 F on the spheroidization of cementite. Nital etched, approximately 500X.

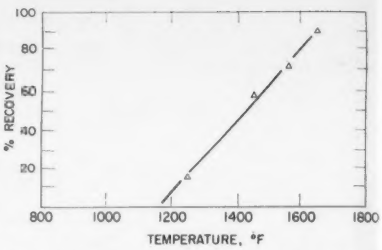


Figure 8—Recovery as a function of temperature for steel initially having 81.5 percent H.A.

of ductility, caused the yield point to reappear.

Even though ductility had been restored almost to its initial value, microstructures of such material still contain grain boundary fissures and voids. Figure 9 shows photomicrographs of an attacked specimen (81.5 percent), which had been given no recovery treatment. Figure 10 shows the structure of an identical specimen which had been given a recovery treatment of one hour at 1650 F. Although the recovered material still shows grain boundary fissures and voids, these are fewer in number and essentially isolated from one another as compared to the greater number of fissures which form an interconnecting network in the unrecovered specimen. Also, there appears to be a greater amount of carbides in the recovered specimen.

It was conclusively demonstrated that recovery is in no way related to the establishment of a new set of grain boundaries, since restoration of ductility was observed when heat treatments at temperatures below the critical were used (1250 F). Further proof was obtained when the attacked specimen shown in Figure 9 which had been tested in tension was utilized. Both a portion of the gauge length which had been plastically strained and a part of the shoulder which had only undergone elastic strain were given a recovery treatment of one hour at 1650 F.

The results are seen in Figure 11. The gauge length portion of the specimen after recovery is identical to that of the unrecovered condition as seen in Figure 9. The large number of grain boundary fissures and voids still persist and form a continuing network. However, the portion of the specimen from the shoulder shows a structure similar to that of the recovered specimen in Figure 10, whereby this network has essentially disappeared leaving isolated fissures and voids. Therefore, it can be concluded that a new set of grain boundaries in themselves do not cause this recovery and that once attacked material is plastically deformed, it appears that it cannot be recovered.

Iron and Iron Alloys

F-1. Exposures up to and including 500 hours at 1000 F and 700 psi hydrogen pressure caused no effect on ductility and strength properties. In addition, no difference in microstructure between exposed and unexposed specimens was noted. Evidently, the carbon content (0.004 percent) was insufficient to produce any hydrogen attack.

F-2. While exposure times up to and including 90 hours at 1000 F at 700 psi hydrogen pressure produced no effect, those of 150, 160, and 315 hours did result in hydrogen attack. However, the amount of attack was very small, 4 percent, and was the same regardless of the length of exposure time. It is to be expected that with longer exposure times essentially no further amount of attack would occur. Obviously, the amount of carbon (0.032 percent) and distribution of carbides present was such so as only to give 4 percent attack; an advanced state of deterioration could not result.

The microstructure of these attacked specimens (Figure 12) shows almost complete decarburization with isolated grain boundary fissures and large voids. These structures are essentially the same as those observed with material having undergone large amounts of recovery.

F-3 and F-4. Alloys F-3 and F-4 were identical except that 0.10 percent Al was added to the F-3 melt as a deoxidizer. Considering the amount of total oxygen present in the irons, the Al added should have been sufficient to tie up the oxygen as Al_2O_3. Therefore, the only difference between alloys F-3 and F-4 was that oxygen, excluding that minor amount in solid solution, was primarily present as Al_2O_3 in F-3 while it was in the form of iron oxides in the other. Sufficient carbon (0.25 percent) was present in both of these alloys to give an advanced state of attack upon proper exposure. Specimens of both alloys prior to exposure were given identical heat treatments resulting in a fine lamellar pearlitic structure.

Results obtained from specimens of F-3 alloy gave an incubation time of 68 hours as compared to a value of 143 hours with specimens of F-4. Since the heat treatments prior to exposure were identical, this large difference in t_o values cannot be explained by differences in type and distribution of iron carbides. Similarly, although specimens of F-3 had a slightly smaller grain diameter than those of F-4, this difference in incubation times cannot be reconciled on this basis. Therefore, it appears that this difference in behavior to hydrogen attack must be related to the difference in the type of oxides present in the alloys and this will be discussed shortly.

Discussion

From Figure 4, it has been shown that below the minimum (between 1000 F and 1100 F) in the $\ln t_o$ vs. $1/T_E$ curve, one rate controlling process is in operation while above this temperature a competing process acting in the opposite direction becomes evident. Attention will first be focused on the sequence of events occurring below this minimum from which a proposed model of hydrogen attack will evolve. The competitive process acting above 1100 F can then be examined.

The data accumulated as to the effects of T_E and P_E clearly demonstrate that the rate controlling process is associated with the incubation or start of hydrogen attack. However, this process itself may not be the embrittling agent involved in this phenomenon.

Embrittlement Stage

The repeated observation that hydrogen attack is accompanied by internal decarburization and the data on alloys F-1 and F-2 in which insufficient amount of carbon was present to produce a state of advance deterioration, suggest that the embrittling agent is methane gas in grain boundaries which acts to weaken the cohesive strength. As methane accumulates in the boundaries, since it essentially cannot diffuse out of the material[8],

pressures can build up to sufficiently large values to actually rupture the boundaries* and create fissures or voids. Also, its pressures can be such as to act only as stress concentrators which upon subsequent application of external loads will cause premature failures, embrittlement. Thus, boundaries containing methane acting as stress concentrators will become ruptured and appear as fine fissures in metallographic specimens due to the applied loads in their preparation.

The methane gas results from internal decarburization in the boundaries in which

$$2H_2 + C = CH_4. \qquad (4)$$

Although this reaction probably takes place in steps, the overall process is as written above. Hydrogen which diffuses in the atomic or protonic form, recombines into molecular form in grain boundaries where there is sufficient room to accommodate it. Carbon diffuses to the grain boundaries, the driving force being a concentration gradient between the carbon reservoirs of cementite and the boundaries themselves which have become depleted due to the decarburization of carbon initially in their vicinity. Because of the size of the reaction product, this reaction essentially takes place in grain boundaries.

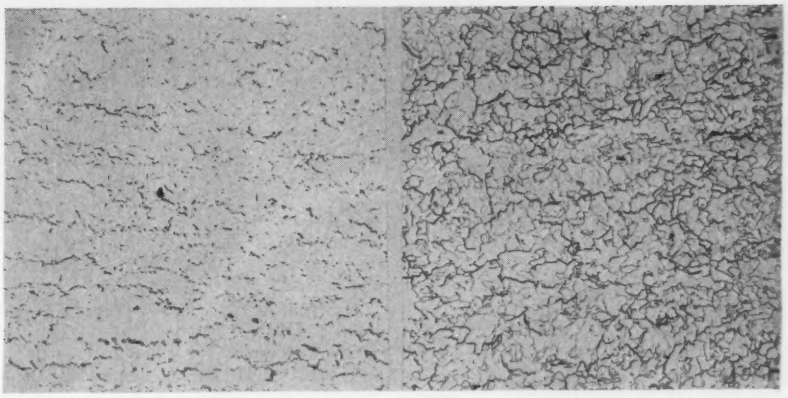
The data observed with alloys F-1 and F-2 clearly indicate that a minimum amount of carbon, which in turn produces a minimum amount of methane gas, is needed to produce any embrittlement. Furthermore, a still larger amount is necessary to produce an advanced stage of attack. In addition, recovery experiments have shown that while the steel was almost completely internally decarburized and that grain boundary voids and fissures existed (Figure 10), the material still had excellent ductility.

The essential difference between almost fully recovered (Figure 10) and unrecovered (Figure 9) material is the fact that in the latter case, the grain boundary voids and fissures formed a continuous network while in the former case they were comparatively isolated. Therefore, this suggests that the necessary and sufficient condition for hydrogen attack is a minimum amount of methane gas in the grain boundaries so distributed as to provide a continuous network of voids, fissures, and/or stress concentrators. Such a distribution appears synonymous with having a carbon content above a minimum amount. This is analogous to cases where a brittle phase (i.e., sulfur in nickel, lead in gold, bismuth in copper) at grain boundaries acts as the embrittling agent, the continuous nature of such a phase being an essential condition.[9]

On the basis of this model of the embrittlement stage in hydrogen attack, observations of this study can be extended. Regardless of the rate controlling process of this stage, it seems apparent that temperature should affect attack rates. However, as was mentioned earlier, there are insufficient data to definitely establish any such effects and in the small temperature range studied, one would not expect large effects to be observed. Hydrogen pressure will only influence attack rates if the rate determining step is one in which hydrogen is involved in a chemical reaction, such as internal decarburization. Since no significant effect of pressure on attack rates was observed, it appears conclusive that either carbon diffusion or carbide dissolution is rate controlling in this embrittlement stage of attack.

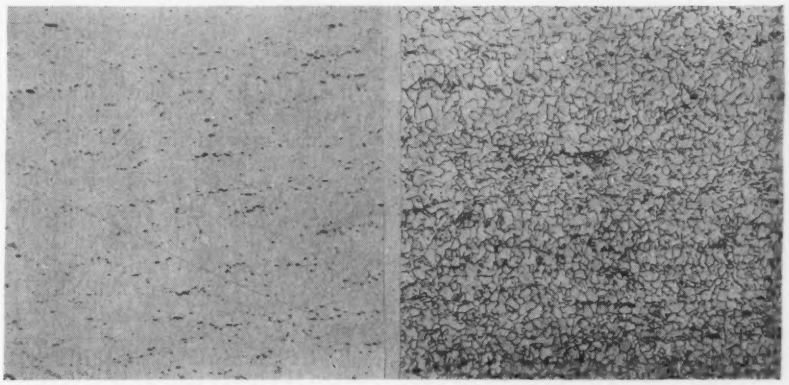
The shape of the attack versus exposure time curves in which there is an initial steep rate followed by a transient and finally a steady state rate can be qualitatively explained by this model. Once embrittlement can take place, the depletion of carbon in the vicinity of the boundaries would set up steep concentration gradients resulting in large amounts of carbon, away from the boundaries, diffusing to them in short periods of time. Events such as these would lead to an initial steep rate of attack over a short time interval. With further time, depletion of carbon reservoirs would cause carbon to diffuse over much longer distances and hence, a decreasing rate of embrittlement. Finally, with almost complete decarburization, the rate would level out into a low steady state condition.

In carrying out recovery treatments on attacked material, the temperatures were such that methane gas breaks down into hydrogen and carbon; this dissociation or cracking is dependent on methane/hydrogen concentration and temperature.[10] It is thought that in those grain boundaries which did not rupture, methane dissociates resulting in a structure in which this network of stress concentrators is broken up and thereby restores ductility. Towards the limit of full recovery, the dissociation of methane will be such as to give only isolated grain boundary voids and fissures as was seen in Figure 10. Most of these are probably the boundaries that actually have been ruptured by methane during attack. Since yield point is dependent on carbon in solid solution, the reappearance of the yield point in recovered specimens adds further evidence as to the breakdown of methane during recovery. The fact that the yield point was observed with specimens recovered at 1250 F for short periods of time while it does not occur



A—As polished, 50X B—Nital etched, 100X

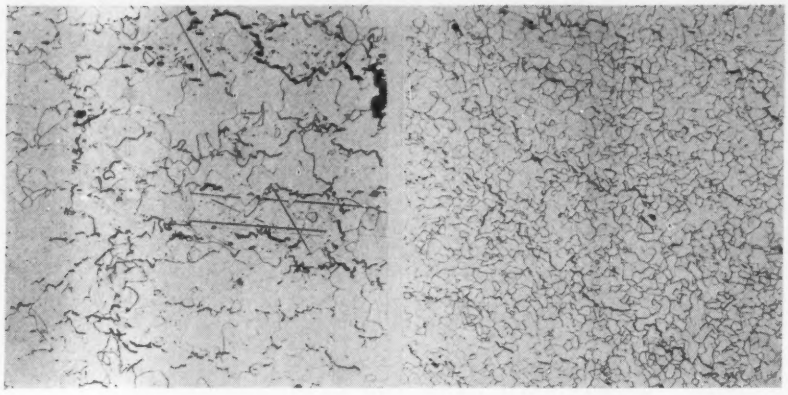
Figure 9—Microstructures of steel attacked 81.5 percent.



A—As polished, 50X B—Nital etched, 100X

Figure 10—Microstructures of steel attacked 81.5 percent followed by 90 percent recovery at 1650 F.

* Thermodynamic calculations show that methane fugacities in the grain boundaries will be in the range 10^6 to 10^9 atmospheres. A conservative estimate of equivalent pressures is a range from 10^6 to 10^8 atmospheres. Pressures such as these would be sufficiently large to weaken and/or rupture boundaries.



A—Gauge length B—Shoulder

Figure 11—Microstructures of a tensile specimen attacked 81.5 percent, tested to fracture and subsequently given a recovery treatment at 1650 F. Nital etched, 100X.

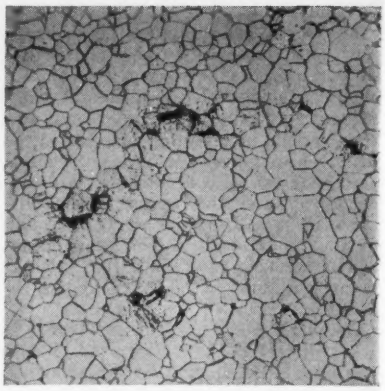


Figure 12—Microstructure of a specimen of alloy F-2 attacked 4 percent after exposure of 160 hours at 1000 F and 700 psi hydrogen pressure. Nital etched, 100X.

in specimens attacked during exposures at 1200 F for 120 hours or more precludes the possibility that its reappearance was due to carbon redistribution during recovery treatments. Also, it is to be expected that attacked material plastically deformed will not recover (Figure 11a) since the stress concentrators (methane in the boundaries) that were present prior to deformation have resulted in a network of grain boundary ruptures during straining. Subsequent dissociation of this methane will not restore ductility.

Incubation

Having proposed a model for the embrittlement stage in hydrogen attack, the rate controlling process governing the initiation or incubation of attack remains to be examined. The experimentally observed relationship of $t_o \alpha P_E^{-3}$ would be in direct conflict to simple diffusion of carbon or hydrogen, the decarburization reaction or carbide dissolution acting in a rate determining capacity. Thus, all these processes can be ruled out as that controlling incubation. Furthermore, this unusual power to which P_E is related to incubation time suggests that the rate determining process is one of a chemical reaction involving hydrogen.

From the results obtained with alloys F-3 and F-4, it is apparent that oxides in the iron play an important role in this rate process. It is well known that Al_2O_3 in iron and steel will be randomly distributed throughout the material, while iron oxides predominantly will be found segregated at grain boundaries. Therefore, grain boundary iron oxide concentration will be much greater in F-4 alloy than in F-3.

Further evidence as to the influence of grain boundary iron oxides on incubation time was obtained in a series of experiments in which approximate incubation times were determined for a killed and semi-killed steel utilizing bend tests. Hydrogen attack was considered to have occurred when the samples did not withstand a bend of 180 degrees. Since structure including ferritic grain size of the two steels was the same, the principal difference between these steels was the fact that iron oxide concentration at grain boundaries should be much greater in the semi-killed than in the killed steel. At 1000 F and 700 psi hydrogen pressure, incubation time for the killed steel was found to be about 30 hours, in good correlation with the tensile experiments, while for the semi-killed steel t_o was $>$ 165 hours. Thus, from these results on both iron alloys and steels, it can be concluded that incubation time for hydrogen attack is directly dependent on the concentration of iron oxides present at the grain boundaries.

With this background, the proposed model for the rate process governing incubation of attack is the reduction of grain boundary iron oxides by hydrogen to form water vapor, which acts as an inhibiting or poisoning agent to the accumulation of methane (Equation (4)) in the boundaries. This model is described as follows:

$$(1)\quad Fe_2O_3 + 3H_2 = 3H_2O + 2Fe \qquad (5a)$$

and/or

$$Fe_3O_4 + 4H_2 = 4H_2O + 3Fe \qquad (5b)$$

$$(2)\quad H_2O + CH_4 = CO + 3H_2 \qquad (6)$$

Since it has been shown that CO diffuses through iron,[8,11,12] probably at an enhanced rate along grain boundaries, it will not accumulate and act as an embrittling agent. In addition, water vapor formed in the boundaries, Equation (5a) and (5b), also will not act as an embrittling agent since it immediately reacts with the methane. Hence, once all the grain boundary iron oxides are reduced and the resulting water vapor consumed by reacting with methane, the latter becomes stable in the boundaries and the onset of the embrittlement stage of attack occurs.

The reaction rate, V_R, of Equation (6) which is the rate determining step for incubation, is given by:

$$V_R \alpha P_{H_2O} P_{CH_4}. \qquad (7)$$

From Equation (5a) or (5b) it is found that

$$P_{H_2O} = K P_{H_2} \qquad (8)$$

and assuming that equilibrium exists in Equation (4)

$$P_{CH_4} = K' P_{H_2}^2. \qquad (9)$$

Substituting (8) and (9) into Equation (7) gives:

$$V_R \alpha P_{H_2}^3. \qquad (10)$$

Thus, the reaction rate of this proposed controlling process is proportional to the third power of hydrogen pressure. Since t_o is inversely proportional to V_R and assuming equilibrium between external and internal hydrogen pressure, it is seen that Equation (10) is equivalent to the experimentally observed result of $t_o \alpha P_E^{-3}$.

On the basis of this suggested model controlling incubation of attack, the observed effects of grain size, surface preparation, specimen size and additivity can be reconciled. Increasing the grain diameter of the material will in turn increase the concentration of grain boundary iron oxide concentration, since boundary area has decreased while total iron oxide content remains constant. Therefore, a longer time—increased incubation time—is needed in order for all the iron oxides to be reduced and the resulting water vapor removed by reacting with the methane. It follows then, that additivity of exposure time is a natural consequence of a process in which reactants, grain boundary iron oxide and water vapor, are consumed (incubation) and of a process in which a reaction product, methane, is being accumulated (embrittlement). Non-exposure intervals will have no effect on consumption or accumulation, except in the case of the latter when these intervals occur at high enough temperatures as to break down accumulated methane. Similarly, surface preparation and specimen size will have no influence on incubation time, since in no manner are these variables involved in this rate controlling process governing incubation.

Attack Above 1000 to 1100 F

Returning to the temperature range above 1000 to 1100 F, discussion can now

be made of the competitive process coming into play causing an increase in t_o with increasing T_R. As was mentioned previously, the results of the experiments on prespheroidized specimens indicate that this competitive process is the spheroidization of cementite.

As is well known, cementite in spheroidal form is more stable than in a plate-like shape due to the decrease in interfacial energy and surface area. It has been shown[13] that volume growth rates of precipitates are governed by their shape and that flat discs will have the fastest rate, spheres the slowest and long cylindrical rods an intermediate rate. The rates for discs, rods and spheres are directly proportional to time to the 5/2, 2 and 3/2 power, respectively. Assuming that in the solid state, diffusion is rate controlling for both growth and dissolution, it would be expected that dissolution rates would be governed by the shape of the particle and have a similar dependency as shown in growth. Thus, spheroidal cementite is expected to have a slower dissolution rate than plate-like cementite in lamellar pearlite. Since in practice the degree of spherical symmetry is dependent upon the degree of spheroidization, the dissolution rate will be dependent on the latter until perfect spherical symmetry is achieved. Furthermore, as the degree of spheroidization increases, coalescence takes place reducing total surface area which in turn decreases the total amount of carbon going into solution.

In order to initiate attack, it has been proposed that the iron oxides at the grain boundaries must be reduced with the resulting water vapor being removed by reacting with methane before the latter can act as an embrittling agent. The rate of methane formed in the boundaries is controlled by either carbon diffusion or carbide dissolution in material having normal pearlitic structure. If this rate of methane formation is decreased, it should be reflected in an increase in incubation time for attack. Just such a situation seems to have occurred in the experiments in which t_o was increased with increasing degree of spheroidization, all other factors being held constant. Thus, it appears that with a spheroidized structure, dissolution rate of the spheroidal cementite definitely is controlling the rate of methane formation.

As the degree of spheroidation is increased, incubation time increases since longer times are necessary in order to produce the methane needed to react and remove the vapor resulting from reduction of grain boundary iron oxides. Although it might appear that water vapor in the boundaries may act as an embrittling agent, thermodynamic calculations show that at these temperatures, pressures would only be in a range from 10 to 10^4 atmospheres. Such pressures should not act to weaken or rupture the boundaries. Thus, carbide dissolution becomes the rate controlling process for both incubation and embrittlement.

Therefore, if at temperatures above 1000 to 1100 F spheroidization is occurring before all the iron oxides are reduced and water vapor removed, the methane production and in turn incubation of attack will be retarded. The degree of spheroidization that has occurred must be such as to change the rate determining step governing incubation to that of spheroidal cementite dissolution.

Alloy and iron-alloy carbides tend to be nodular or spheroidal in shape even within pearlite colonies, as well as being more stable relative to cementite. Thus, carbide dissolution should be the rate determining process for both incubation and embrittlement in these alloy steels and it follows that such alloy steels should be much more resistant to hydrogen attack than plain carbon pearlitic steels. In addition, the possibility exists that the presence of these alloying elements in or near the boundaries has an inhibiting effect on methane formation thereby further increasing resistance to attack. Just such observations have been recorded for it has been well established[3,6,12,14] that additions of carbide stabilizing and carbide forming alloy elements afford steel good protection from hydrogen attack, while noncarbide formers (nickel, silicon and copper) have been found to be completely ineffective.[6]

Summary

The kinetics of hydrogen attack of a killed steel have been studied in the temperature range 800 to 1200 F and in the pressure range of 450 to 950 psi hydrogen. The effects of time, exposure temperature, hydrogen pressure, structure, grain size, surface and size have been investigated from which a quantitative relationship between incubation time of attack and temperature and pressure was obtained. It was also demonstrated that recovery of attack material can be achieved.

From the results observed with the steel and from those obtained from a series of high purity iron alloys, a model for hydrogen attack has been proposed which satisfactorily describes the observations of this investigation. In this model, the rate process controlling incubation of attack is the reduction of grain boundary iron oxides resulting in water vapor which acts as a poisoning agent to the accumulation of methane in the boundaries. After the water vapor is removed by reacting with methane, the latter acts as an embrittling agent when its pressures result in a continuous grain boundary network of fissures, voids, and/or stress concentrators. Stabilizing the carbides (spheroidizing, alloying, etc.) increases the resistance to hydrogen attack as carbide dissolution becomes the rate determining process for both incubation and embrittlement.

Acknowledgments

This study was conducted in the Materials Development Laboratory of the Esso Research and Engineering Company. The author wishes to express his appreciation to Esso Research and Engineering Company for permission to publish this paper and to Professor John O'M. Bockris, and Professor Maxwell Gensamer and Mr. A. R. Ciuffreda for their stimulating discussions and helpful suggestions. The author is indebted to Mr. Joseph Vallone for carrying out the metallographic work necessary in this investigation.

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Any discussion of this article not published above will appear in June, 1961 issue.

Massive De-Aluminization of Aluminum Bronze By Chloride Crevice Attack*

By L. W. GLEEKMAN and R. K. SWANDBY

Abstract

The failure of a wrought aluminum bronze drum (6 to 8 percent aluminum and 1.5 to 3.5 percent iron) drying a calcium carbonate paste was established as due to de-aluminization. The selective attack occurred not only along the 7'-6" longitudinal weld where two phases were present but also along the entire periphery of the 250 fins machined into the outer face of the drum. These fins were all single-phase material. The drum had been in service only a year when many fins broke off. The calcium carbonate paste was essentially neutral (pH 8.0), containing only 0.2 percent NaCl and Na_2SO_4 as minor impurities. Saturated steam was used inside the drum at 350 F. Associated with the failure was a hardened deposit of $CaCO_3$ and $CaSO_4$ acting as a crevice around the fins and in the grooves.

Laboratory tests, using a sandwich assembly of the same aluminum bronze with the various combinations of $CaCO_3$ and liquids as the filling and with heat transmitted through one surface of the metal, established that de-aluminization occurred only with chloride present in the crevice. No attack occurred with the chemically pure $CaCO_3$ and distilled water or $CaSO_4$ and water. The ultimate solution was to switch to 90-10 cupro-nickel wrought plate welded with 70-30 cupro-nickel; this has given satisfactory service for two years, with no signs of attack. 6.3.6, 3.6.2

Introduction

THIS PAPER concerns the problem encountered in the drying of a calcium carbonate paste containing a small amount of chloride ion, described in terms of the deterioration of a wrought aluminum bronze drum used as a fin drum drier. The term "massive" is used in the title to point out that the de-aluminization of this aluminum bronze drum occurred over the entire periphery of the drum which was 3 feet in diameter and 7½ feet long, with approximately 250 fins machined into the face of the drum. The metallurgical structure of the aluminum bronze was alpha phase throughout except for the longitudinal weld which had a two phase structure.

Schussler and Napolitan[1] attributed the failure of aluminum bronze to selective corrosion of the aluminum-rich phase in an aluminum-silicon bronze having a duplex structure. Their studies with single and two-phase aluminum bronze in aqueous hydrofluoric acid showed that the alpha bronzes suffered no harmful attack, while the duplex bronzes, regardless of their heat-treated structure, suffered selective de-aluminization attack.

Williams[2] reported that de-aluminization was caused by the corrosion of the alloy and redeposition of the copper *in situ*, pointing out that the process is analogous to dezincification in brasses. He indicated that de-aluminization had been observed to some extent in wrought alloys with 6.5 to 11 percent aluminum and with 9 to 11 percent aluminum, whereas an alloy with 6 to 8 percent aluminum plus 3.5 percent iron was reported as not subject to de-aluminization. He further reported that de-aluminization is sometimes found where crevice corrosion attack had occurred. This work was specific to sea water corrosion.

The structure of aluminum bronze, especially the form and distribution of the beta constituent, most probably has an important influence on the extent of de-aluminization.[3] According to McKay and Worthington (as cited in reference 3), duplex aluminum bronze alloys are considered inferior to the homogenous alloys for corrosion-resisting purposes.

Hallowes and Voce[4] reported de-aluminization of 10 percent aluminum bronze from steam containing small amounts of SO_2 at 400 C after 70 hours in a laboratory test. Steam at the same temperature containing small amounts of free chloride also produced de-aluminization.

One of the more standard methods of producing calcium carbonate (a material widely used as a filler and pigment for paint, rubber, and many other commodities) is to mix sodium carbonate (soda ash) and calcium chloride solutions, precipitating calcium carbonate. This product, after purification, is separated from a slurry and is then dried in one or more stages. The experiences of the authors' company indicates the desirability of using a rotary fin drum upon which paste from a filter falls removing the excess free moisture, and finally drying the calcium carbonate in a tunnel dryer to negligible moisture content.

For many years a rotary fin drum drier made out of centrifugally cast silicon bronze was used. The drum was heated from the interior by 125 psig saturated steam to a temperature of 350 F. Because of the combination of corrosion and deterioration problems from the moderately high temperature and the calcium carbonate paste, several silicon bronze drums cracked in service. Also, the relatively low coefficient of thermal conductivity of silicon bronze and the difficulty of procuring sound castings indicated an alternate material of construction was desirable.

An economic survey of potential materials of construction established that a cylinder could be fabricated from a

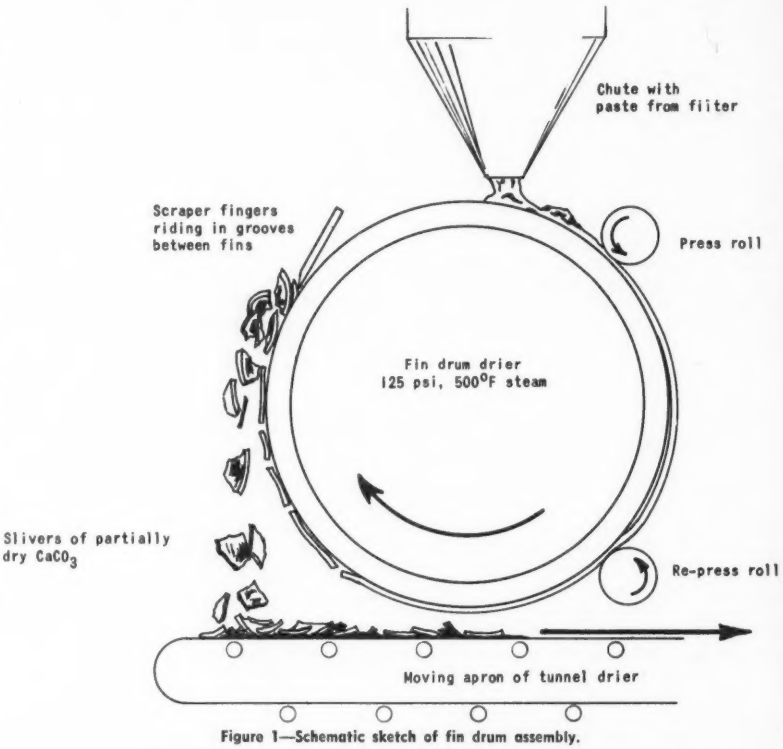
Chute with paste from filter
Scraper fingers riding in grooves between fins
Press roll
Fin drum drier
125 psi, 500°F steam
Slivers of partially dry $CaCO_3$
Re-press roll
Moving apron of tunnel drier

Figure 1—Schematic sketch of fin drum assembly.

★ Submitted for publication August 2, 1960. A paper presented at a meeting of the North Central Region, National Association of Corrosion Engineers, Milwaukee, Wisconsin, October 19-20, 1960.

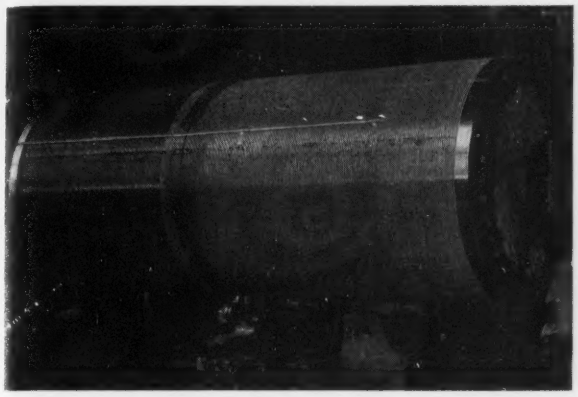

Figure 2—Overall view of attacked drum in partially remachined condition.

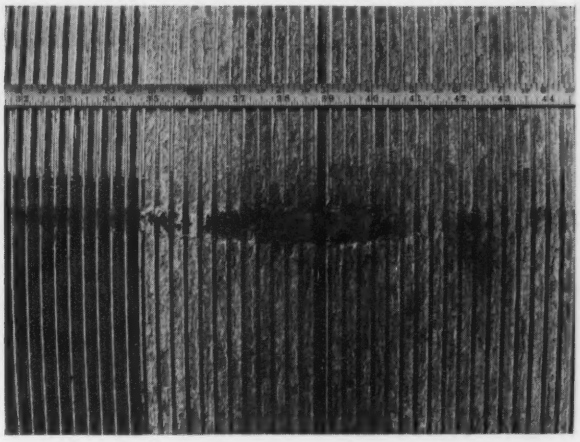

Figure 3—Close-up of fins and welds showing heavily de-aluminized section of weld. Fins were partially cleaned out by machining.

Swandby

Gleekman

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wrought plate with a longitudinal weld less expensively than it could be made as a centrifugal casting. On this basis, a survey of physical and thermal properties of potential materials of construction was made, which is shown in Table 1.

Aluminum Bronze D was selected over the original silicon bronze for the construction of the fin drum because of the following properties:

1. High maximum allowable stress at 500 F.
2. High thermal conductivity compared to other alloys.
3. Excellent weldability and machineability.
4. Excellent economics.

A schematic sketch of the fin drum assembly is shown in Figure 1. The actual production conditions are essentially the following:

1. Calcium carbonate paste from the filter wheel, containing 50 percent excess moisture with 0.2 percent NaCl and $CaSO_4$ (wet basis), falls on the fin drum at top center.

2. The drum rotates approximately 45 degrees where the cake is pressed into the hot fin drum surface. Saturated steam at 125 psig and 350 F is introduced continuously to the interior of the rotating drum. After rotating an additional 90 degrees, the cake is repressed into the fins for maximum contact with the heated surface. A further 180 degree rotation to within approximately 45 degrees of the top brings the relatively dry cake to the fingers. These fingers ride in the grooves between the fins and remove the slivers of relatively dry calcium carbonate. The temperature of this material is approximately 212 F. Since this is a continuous operation with an unsteady rate of feed of the paste to any one part of the drum, parts of the fin drum can be overheated from no paste falling on it, while other parts can be cooler by being continually in contact with the wet paste.

It was recognized that there was a possibility of chloride carry-over from the reaction tank, where the calcium chloride solution is mixed with the soda ash. For that reason, none of the stainless steels were chosen; in addition, they had poor thermal conductivity and relatively high cost. The alkalinity of the partially dried paste (pH 8.0) on the drum restricted the use of aluminum alloys, while the poor strength of copper at the operating temperature eliminated its use in spite of its excellent coefficient of thermal conductance. Small amounts of free ammonia could be present in the calcium carbonate solution carried over with the $CaCl_2$ solution: this was not felt to be critical insofar as stress corrosion cracking of a copper-base drum was concerned since the temperature of the drum would cause the ammonia to be driven off from the paste.

Subsequent reappraisal of possible materials has led to consideration of a steel

TABLE 1—Comparison of Wrought Metals for Fin Drum*

Metal**	ASME Code	Minimum Physicals		Maximum Allowable Stress, psi				Thermal Conductivity***	1955 Costs for 1" Plate x 8' x 10'
		T.S.	Y.S.	350 F	400 F	450 F	500 F		
Aluminum Bronze D	SB-169	70,000 psi	30,000 psi	15,000	14,500	12,000	10,000	552	77 cents/lb.
Silicon Bronze	SB- 96	50,000	18,000	5,000	.....	.....	.....	252	76.62
Copper	SB- 11	30,000	10,000	3,800	2,500	.....	.....	2,352	67.13
90-10 Cupro-Nickel		40,000	15,000	9,000	8,700	8,300	7,500	324	84.76
80-20 Cupro-Nickel		50,000	18,000	10,700	10,300	10,000	9,500	240	.....
70-30 Cupro-Nickel	SB-171	50,000	20,000	12,000	11,700	11,300	11,000	204	97.09
Monel (hot rolled)	SB-127	75,000	40,000	.....	17 000	.....	17,000	180	100.00
Inconel (hot rolled)	SB-168	85,000	35,000	.....	20,000	.....	20,000	104	.....
2½% Ni-Steel	SA-203	75,000	.....	.....	.....	.....	17,500	465	.....
Type 316L Stainless	SA-167	75,000	.....	.....	17,500	.....	17,200	116	80.00

* Date from Table NF-2, ASME Boiler and Pressure Vessel Code, 1956, except for costs.
** Annealed unless indicated.
*** Btu/ft²/hr/°F/inch.

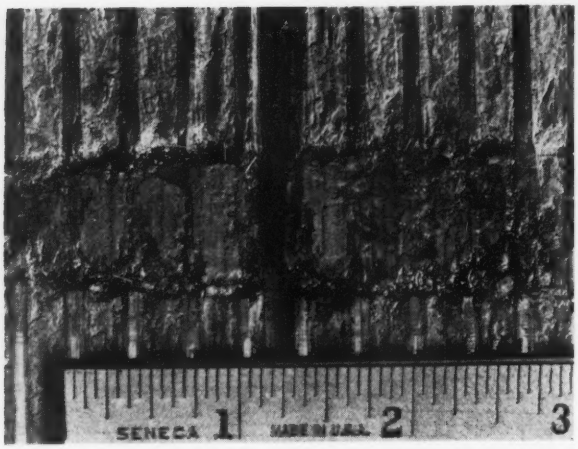

Figure 4—Close-up of re-deposited copper at weld.

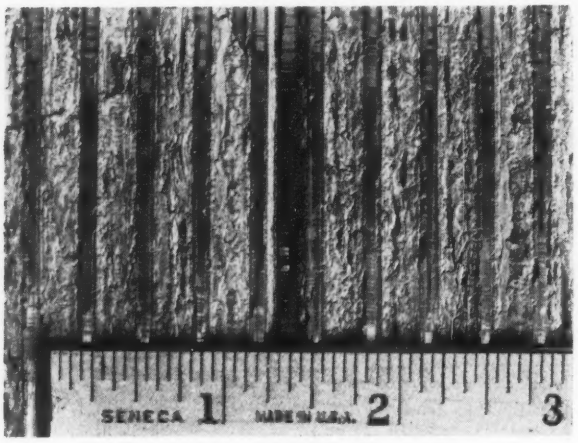

Figure 5—View of fins 180 degrees opposite weld, showing de-aluminization of edges of fins.

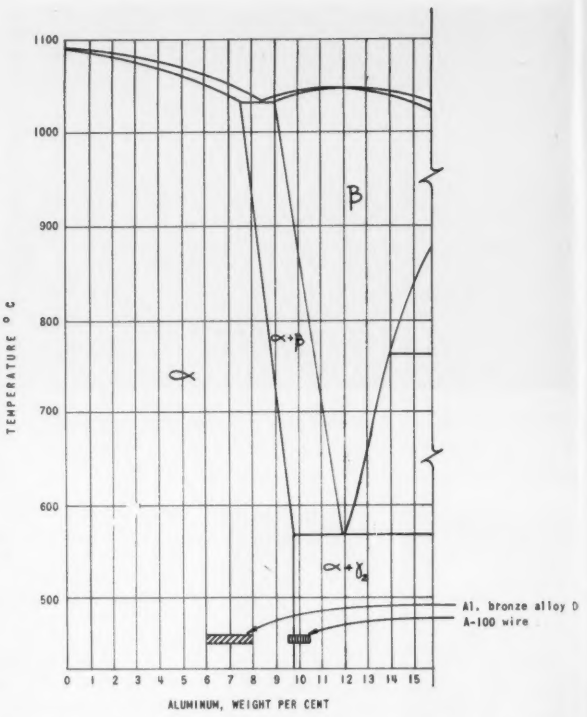

Figure 6—Standard aluminum-copper phase diagram (from Metals Handbook. American Society for Metals, 1948 Edition, p. 1160).

drum where surface treatments after fabrication may provide suitable protection from rusting and pitting.

Analysis of Failure

A drum of aluminum bronze, meeting ASTM specification B-169 Alloy "D", was constructed by a major metal fabricating concern. Its analysis, along with the analysis of Type A-100 bronze wire which was used for the longitudinal weld, is shown in Table 2.

The fabricator reported the following steps and observations: After rolling to the desired shape and automatically welding the longitudinal seam, the drum was stress relieved at 1175 F for 1½ hours and was then air-cooled. Following the stress relieving, the machining operation was carried out, the first step being a true-up operation. The grooves were then machined with a gang tool using automatic feed and no coolant. The finish cut on each groove was made by manual feed, using lard oil as the coolant to obtain an F-3 finish. A review of the X-ray films showed that the welding was better than that required by the ASME code; there was no evidence of cracking, undercutting, or slag inclusions.

The drum was operated at approximately 90 percent daily efficiency (shut down approximately 3 to 5 days per month as normal outage). After approximately one year, operation of the drum showed that carbonate was peeling off in lumps rather than in slivers. It was subsequently established that the grooves were filled with a hardened calcium carbonate scale and that the fingers were not removing the dried product. A check of the operational history of the drum established that it had been acid washed three times in its history, using approximately 15 percent muriatic acid each time.

The condition of the drum as removed at this time, is shown in Figures 2, 3, 4 and 5. Figure 2 is the over-all view of the drum in partial stages of remachining, and Figure 3 is a close-up of the partially machined fins and grooves at the weld. In Figure 4 is shown the heavy amount of de-aluminization and redeposition of the copper at the weld. To establish that the de-aluminization was occurring over-all, other than adjacent to the longitudinal weld, Figure 5 is a view 180 degrees opposite to the weld, showing the partially machined groove 39 inches from the end.

Examination of the drum, as can be seen from the above figures, showed excessive corrosion occurring at the longitudinal weld area and also along the surfaces of the fins. In the course of remachining the drum, a corroded fin was removed and compared with uncorroded material which had only the oxide film removed. Table 3 shows the difference in analyses. The calcium carbonate scale machined out from between the fins was analyzed; this showed 36.1 percent sulfates, 5.9 percent chlorides, 3.0 percent copper, and 0.82 percent R_2O_3. A grab sample of the paste falling on the drum showed an analysis of 0.15 percent sulfate and 0.05 percent chloride on a wet basis (50 percent excess water).

Reference to the standard phase diagram (Figure 6) for aluminum-copper indicates that the base material of the

TABLE 2—Analyses of Base Metal and Welding Wire

Element	Base Metal for Fin Drum[1]	Type A-100 Welding Wire[1]
Aluminum	6—8%	9.4—10.2%
Iron	1.5—3.5	0.6—1.2
Zinc	.....	0.2 maximum
Silicon	.....	0.04 maximum
Lead	.....	0.02%
Other Elements	0.5%	.05%
Copper	Balance	Balance

[1] Certified Analyses by suppliers for Code Stamp.

TABLE 3—Analyses of Corroded and Unattacked Fins

Element	Analysis of Corroded Fin Including De-Aluminized Area	Analysis of Unattacked Fin With Oxide Film Removed
Aluminum	4.56%	7.32%
Iron	2.94	3.80
Copper	75.21	88.88

Figure 7—Photomicrograph (100X, reduced to 72X for reproduction) of weld area. Etchant: 100 percent ammonium persulfate.

Figure 8—Photomicrograph (100X, reduced to 72X for reproduction) of base metal. Etchant: 10 percent ammonium persulfate.

Figure 9—Transverse view of de-aluminized weld.

Figure 10—Longitudinal view of de-aluminized weld.

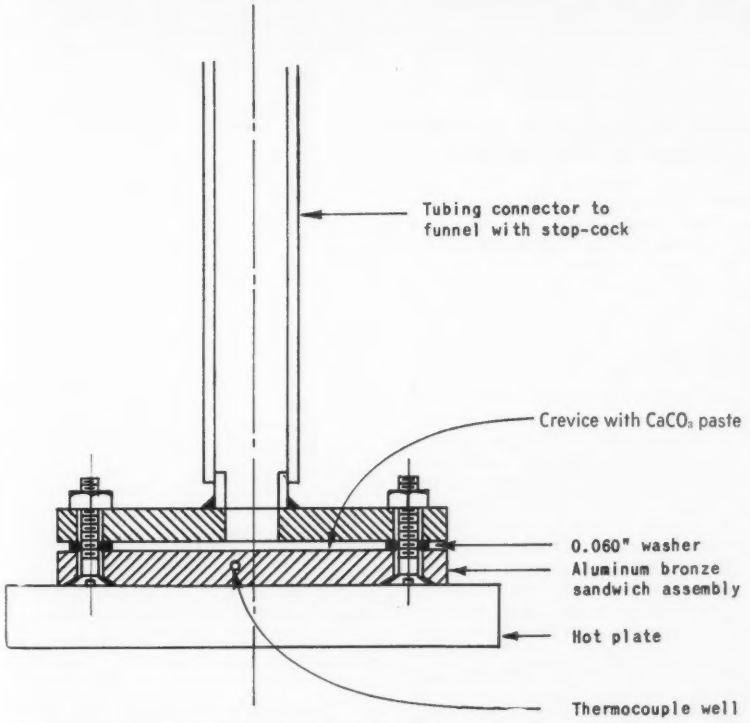

Figure 11—Schematic diagram of sandwich assembly for determination of de-aluminization of aluminum bronze.

fin drum would be in the all alpha region while the A-100 welding rod would be in the region of alpha plus gamma$_2$; this admittedly does not take into account the presence of iron as a third component. The presence of a second phase is shown in the attached photomicrographs. Figure 7 being a photomicrograph of the weld area and Figure 8 being a photomicrograph of the base material.

To more clearly delineate the nature of the de-aluminization, photographs Figures 9 and 10 are attached, which show the fin drum after it had been machined to ⅝-inch minimum wall thickness and subsequently returned to service. This return to service extended the life of the drum approximately 4 months, at the end of which time de-aluminization once more occurred, requiring the drum to be completely removed and scrapped. During this 4 month period there was no acid washing. The presence of the second phase in the micro-structure of the weld area might serve as a suitable explanation for the susceptibility to de-aluminization. As can be seen from the over-all views, however, the entire periphery of the fins showed de-aluminization and no second phase was present in those areas.

Experimental Procedure

To establish the possible mechanism of failure, a simulated aluminum bronze drier was set up in the laboratory. This consisted of two plates of aluminum bronze "D" with a crevice between these plates where calcium carbonate or other materials could be placed as a sandwich filler. Figure 11 is a schematic diagram of this assembly. Heat flowed to the material from a resistance heater below the lower plate while a glass tube, cemented in place, was used to feed the test solution to the chemical between the plates. Four corrodent systems were used: one being chemical purity calcium carbonate plus distilled water, the second being a five percent calcium chloride solution with a pH of 9.1, the third being the calcium carbonate from the plant with the filtrate from the filter wheel, and the

fourth being chemical purity calcium sulfate plus distilled water.

All four sandwiches were held at a temperature 450 F for three days. At the end of the three-day period, the sandwiches were disassembled and the plates examined visually for de-aluminization. In the case of chemically pure calcium carbonate and distilled water as well as the calcium sulfate and distilled water, there was no attack evident: the aluminum bronze still had its initial yellow color. The calcium chloride solution caused severe de-aluminization as shown by the attached photograph Figure 12. The plant calcium carbonate using filtrate from the filter wheel caused light de-aluminizataion.

Discussion

While this sandwich test assembly is not completely inclusive of all the possible materials or combination of materials which could cause attack, it is felt that the test does indicate the de-aluminization more readily occurs in the presence of chloride in a crevice at the elevated temperature. The work of Hallowes and Voce,[4] as cited earlier, closely simulated the conditions of the fin drum in terms of steam with small amounts of chloride producing de-aluminization.

Based on the test results, it is believed that the steam formed during the drying of the calcium carbonate hydrolyzed the calcium chloride according to the following reversible reaction:

$$CaCl_2 + HOH \rightleftarrows Ca(OH)_2 + 2HCl$$

The calcium sulfate scale on the metal surface served as a permeable membrane, allowing the hydrogen chloride to penetrate to the surface of the metal. Since calcium hydroxide is a precipitate and relatively insoluble, it could not penetrate the calcium sulfate scale. The hydrolysis then became irreversible with the hydrogen chloride free to attack the aluminum bronze. Because calcium sulfate is considerably more insoluble than calcium chloride, the possibility of sulfuric acid formation was quite negligible. Hydrogen chloride, therefore, undoubtedly caused the uniform dissolution of both the single and the two phase aluminum bronze alloy. The two phase alloy, however, was more severely attacked than the single phase because of its inherently weaker resistance to corrosion. Following the dissolution, a re-deposition of copper occurred in the same manner as dezincification of brass.

Conclusion

The happy conclusion to this massive de-aluminization of aluminum bronze was the construction of subsequent drums from 90-10 cupro-nickel using 70-30 cupro-nickel as the welding material. These drums have been in operation two years with no evidence of any attack. While the coefficient of heat transfer of the cupro-nickel is somewhat lower than that of aluminum bronze, the improved corrosion resistance and strength properties make the cupro-nickel an ideal material of construction for this service.

The analysis of this failure also points out the importance of minor impurities in solution frequently overlooked when selecting materials of contruction. In this case, only 0.05 percent chloride and 0.15 percent sulfate were the trouble makers in the calcium carbonate paste.

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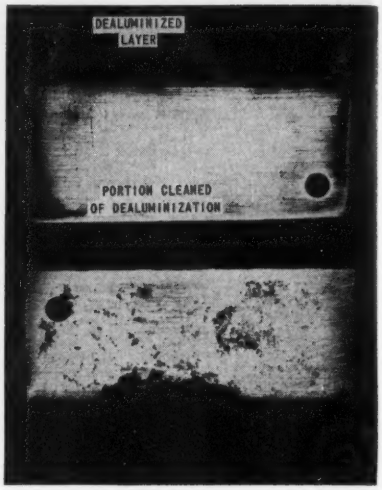

Figure 12—De-aluminized test pieces.

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Any discussion of this article not published above will appear in June, 1961 issue.

Cathodic Protection and Zinc Grounding In Industrial Plant Construction*

By J. D. GHESQUIERE

Abstract

This paper relates the problems of corrosion and grounding in the construction of a large manufacturing facility. The elimination of copper ground rods, which cause galvanic corrosion problems and unusual cathodic protection current requirements, is discussed. The design considerations are reviewed for a cathodic protection system installed during the construction of this industrial facility as well as the selection of zinc rods for grounding purposes. Test data obtained upon completion of the cathodic protection system are presented 5.2.1

Introduction

THIS PAPER covers the effect of the copper grounding system on the design of a cathodic protection system for the underground facilities associated with the construction of a new industrial plant. It also illustrates the area in which a corrosion engineer can play an important role during the design of a major installation.

Various authors have reported that when copper is connected to steel in soil, excessive current is required to provide protection to the steel. On previous occasions, it had to be noted that the association of copper increased the current requirements from 10 to 30 times. To the author's knowledge, no explanation or analysis of this unusual requirement has appeared in the literature. In this paper, an attempt will be made to analyze and show how these unusual currents can be estimated.

Industrial Plant Facilities

The Chrysler Corporation St. Louis Assembly Plant, Fenton, Missouri includes the assembly plant proper, administrative building, boiler house, oil and paint storage building, underground tank farm, acetylene and oxygen storage, sewage oxidation lagoons, and industrial waste treatment plant with 2-section effluent lagoons. The total building area is approximately 1,575,000 square feet.

The underground off-site piping, which was provided by the utility companies, for domestic cold water and gas services, is pre-stressed concrete and steel pipe, respectively. The steel pipe gas main is under cathodic protection by the local gas company. High voltage electric power service is supplied to the plant site on overhead lines by the local power company.

Within the site area, the power company continued the high voltage power service on overhead lines to the sub-station adjacent to the boiler house. This service is connected to the switchgear inside of the boiler house; the low voltage cables are installed underground therefrom to serve the various buildings. In addition to the utilities, the tank farm consists of eight 20,000 gallon and four 15,000 gallon capacity miscellaneous oil storage tanks installed underground. The fire protection system, in conjunction with the domestic cold water system, comprises a 400,000 gallon elevated water tank and two 750,000 gallon ground suction tanks with associated piping. The entire plant is looped by an underground cast iron fire protection hydrant and sprinkler service main.

Furthermore, there are also "H-Section" steel piles for building support as well as underground piping of steel and cast iron for water, gas, propane, oxygen, acetylene and oils, all of which have been integrated with the cathodic protection system.

Preliminary Survey

Prior to the start of construction, during the design stages of the plant, a preliminary corrosion survey was performed at the site. The purpose of this survey was to predict whether underground corrosion would be a problem at this location. Soil boring data were examined, soil resistivity tests taken to various depths, pH and redox potential measurements obtained, and tests for stray current performed. It was found that the site contained a wide variation in type of soil due to "cut and fill" operation in preparation of the site. These included clay, sand, silt, cinders, top soil and black muck. The soil resistivity measurements ranged from 900 ohm-cm to 50,000 ohm-cm. The average resistivity at normal pipe depth ranged from 990 to 8500 ohm-cm. The soil was acid in nature, exhibiting a pH of 5.9. The nature of the soil is such that it will not permit good natural drainage. General environments of the soil encountered are favorable to the growth of anerobic bacteria.

Based on these measurements, and observations, previous experience at other locations in the general area and review of the facilities to be installed, including the complex copper grounding system, it was predicted that serious underground corrosion problems could be expected at this location. Leaks in tanks and piping were predicted to occur within 6 to 10 years. Furthermore, corrosion mitigative measures were recommended, including the application of cathodic protection to underground piping, underground tanks, bottoms of on-ground tanks and lead cables.

It was advantageous to design and install the cathodic protection system along with the construction of the plant and plant facilities to realize additional savings, and to co-ordinate the design from the corrosion standpoint to eliminate "built-in" corrosion problems. The necessary bonding of joints to ensure electrical continuity was achieved during installation to eliminate future digging, breaking of concrete, etc. Rectifier power feeds, signal wiring and test point bonds were installed with the original electrical wiring to minimize electrical facility changes, additional runs, etc.

The design requirements for the cathodic protection system were studied and determined. The type of cathodic protection system whether galvanic or impressed was determined, current density required to provide adequate protection, and selection was made of anode material and rectifier locations. One major item which greatly affected the considerations was the use of copper in the grounding system.

Copper Grounding

The proposed electrical copper grounding system for the plant consisted of the normal sub-station grounding mats, individual grounds for each motor, lighting panels, transformer banks, underground tanks, street lights, etc. The electrical grounding proposed consisted of 1 inch × 10 foot copper ground rods. The number of rods was estimated to be over 1,000. Also, the area of bare conductor interconnecting the ground rods was about equal to the ground rods. The total area of bare copper was estimated to be 5,240 square feet.

Electrical grounding systems are historically made from copper ground rods connected together by bare copper conductors. Since the primary purpose of the grounding system is for safety, copper metal has been utilized because it exhibits a long life buried in the soil.

* Submitted for publication September 6, 1960. A paper presented at a meeting of the Western Region, National Association of Corrosion Engineers, San Francisco, California, October 6-7, 1960.

About the Author

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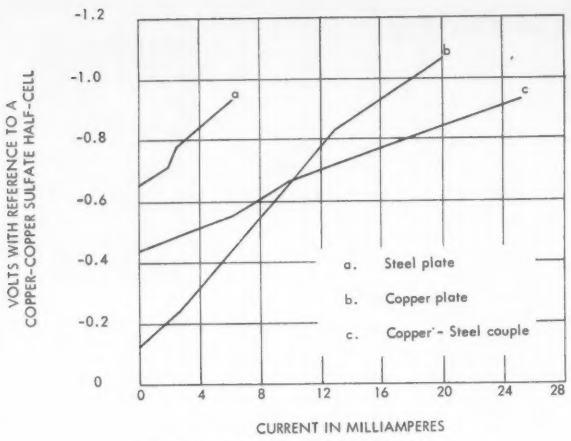

Figure 1—Current-potential relationship.

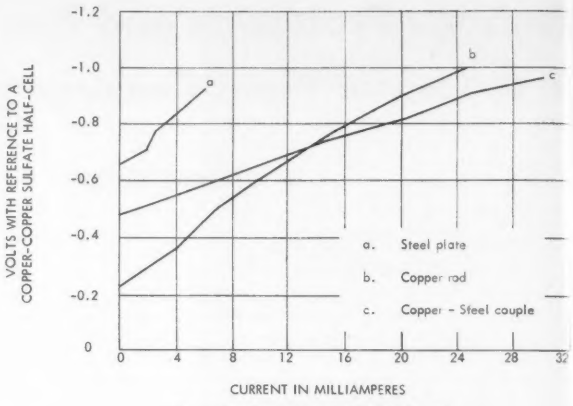

Figure 2—Current-potential relationship.

Copper is a very noble metal and has a low hydrogen over-voltage, and thus may cause a serious galvanic corrosion problem when electrically connected to a less noble metal. It is a common practice in industry to tie all underground metallic structures into the electrical copper grounding system. This practice can result in serious corrosion activity on underground iron and steel pipes, steel tanks and lead cables. The degree of the corrosion due to the use of dissimilar metals, when electrically connected in an electrolyte, is dependent on a number of factors:

1. The relative exposed area of the cathode to that of the underground structure (i.e., large cathode [copper] and small anode [underground metal] will promote serious corrosion activity on the anode).

2. The soil resistivity surrounding the metals (i.e., low resistivity will allow large corrosion currents to flow from the anode to the cathode with corrosion occurring at the anode).

3. The potential difference between the metals (i.e., the greater potential will tend to cause more current to flow, resulting in additional corrosion activity).

The corrosion problem, due to connection of the copper ground to the underground metal, regardless of the soil resistivity and potential difference, is frequently greatly magnified because of the coating on the metal. A similar case is the lead sheathed cable tied into the copper grounding with only a few square inches of lead in contact with moisture in damp underground ducts.

Since it has been determined that cathodic protection would be installed to minimize underground corrosion activity, no estimate was made of the extent of the corrosion effect caused by the copper. However, in order to provide protective currents to the desired structures, it is necessary to raise the potential of the copper to that of the other metals before any protective current will flow to these structures.

In order to assess the effect of the copper on the cathodic protection system, consideration was given to the magnitude of protective current required to change the potential of copper to —0.85 volt (reference $Cu/CuSo_4$ half-cell).

The following consideration, tests and observations were performed to establish a basis for estimating the copper steel couple current requirements.

Effect of Potential Difference On Current Requirements

To evaluate the effect of the potential difference of copper and steel on cathodic protection current requirement, consider a hypothetical case employing these two metals. Assume equal area of copper and steel, and identical shapes in the same electrolyte.

The following potentials, selected as usual potentials, refer to copper-copper sulfate half-cell:

Steel potential = —.65

Copper potential = —.15

In order to provide protection, it is necessary to raise the potentials of both metals to —0.85. Potential change required to:

Change Steel	Change Copper
—.85	—.85
—.65	—.15
.20	.70

Ratio of voltage change is:

$\frac{.70}{.20}$ = 3.5 times the voltage change is required to raise the potential of copper to —.85 as with steel.

I_sR_s = voltage on steel = ΔE_s

I_cR_c = voltage change on copper = ΔE_c

then:

$\Delta E_c = 3.5\ \Delta E_s$

$I_cR_c = 3.5\ (I_s)\ R_s$

$R_s = R_c$ (for same size, shape in the same electrolyte).

then:

$I_c = 3.5\ I_s$

Therefore, for equal areas, shape and same electrolyte, it will require 3.5 as much current to obtain this change in voltage.

Test Performed To Confirm The Above Analysis

One foot square (2 square feet area) of low carbon sheet steel (bare) and one foot square (2 square feet area) of sheet copper (bare) were selected for test specimens. Tests were performed in free flowing 3,000 ohm-cm water at 68 F using an impressed current system with a remote anode (150 feet). Lake St. Clair was selected as test location to eliminate chances of effects of other metals, stray currents, and to provide a large electrolyte (as compared to a small test in a laboratory container).

Table 1 presents the data obtained indicating the currents required to protect the:

a. Steel alone.

b. Copper alone.

c. Copper-steel couple (connected together.

The potentials recorded are negative with respect to $CuCuSO_4$ half-cell, and were obtained using a potentiometer type voltmeter. Figure 1 is a plot of this information.

From Table 1:

Measured steel potential = —.66 without current applied

Measured copper potential = —.12 without current applied

Potential change:

Change Steel	Change Copper
—.85	—.85
—.66	—.12
.19	.73

Ratio of voltage changes measured = $\frac{.73v}{.19v} = 3.84$

Ratio of current measured = $\frac{15ma}{4ma}$ = 3.75

In order to fully evaluate the cathodic protection current requirements of the copper grounding system, the dimensions of the ground rod must be considered. The resistance per square foot of area of pipe or rod varies considerably with the diameter. A small diameter pipe or rod will receive more current per square foot than a large diameter pipe to raise it to the same potential.[1]

Effect Of Relative Current Densities For Different Size Interconnected Pipes

The proposed copper grounding system employed 1 inch × 10 feet copper rods and bare copper conductors connecting the rods, which accounts for approximately 5,240 square feet of bare copper exposed. The underground piping to be protected contained bare and coated 2, 3, 4, 5, 6, 8, 10, 12, 15 and 16 inch pipe.

For estimating current for relative size, an average size of 12 inch diameter pipe was selected as typical diameter of the majority of the pipe, and 1 inch diameter for the size of the copper rods.

Consider the current densities required for one lineal foot of 12 inch and 1 inch diameter pipes, of the same material, for a given voltage change with respect to a remote point (100 feet).

I = total current required for one lineal foot
i = current density in ma/sq. ft.
A = area of one lineal foot of pipe
R = resistance for one lineal foot of pipe

$$R = \frac{.012\rho \log \frac{D}{a}}{L} \quad 1)$$

a_1 = radius one inch rod = 0.5 inches
a_{12} = radius 12 inch pipe = 6.38 inches
L = one foot
$I_{12} = i_{12}A_{12}$
$I_1 = i_1A_1$

for the same potential:

$$I_1R_1 = I_{12}R_{12}$$

Then:

$$(i_1A_1)R_1 = (i_{12}A_{12})\,R_{12}$$

or

$$\frac{i_1}{i_{12}} = \frac{A_{12}R_{12}}{A_1R_1}$$

$$\frac{i_1}{i_{12}} = \frac{(\pi \cdot 12.76)\left(.012\rho \log_{10} \frac{1200}{6.38}\right)}{\pi \cdot 1 \quad \left(.012\rho \log_{10} \frac{1200}{.5}\right)}$$

$\frac{i_1}{i_{12}} = 8.59$ Ratio of current required by one inch rod compared to 12 inch pipe for the same potential change due to difference in resistance.

The above considerations are based on the same metal. When substituting different metals, it will be necessary to alter this ratio to allow for their difference in potentials.

Test Performed To Confirm The Above Analysis

Additional tests were performed to illustrate this phenomenon. It was not practical to perform tests on a 12 inch diameter pipe; therefore, one square foot (2 square feet area) of low carbon steel (bare) and a ⅝ inch × 6 foot copper ground rod were selected. The tests were performed in the same manner and under the same conditions as utilized in illustrating the effect of the difference of potential of metals.

The ratio of current density due to difference in shape of a 12 inch square plate and a ⅝ inch × 6 foot copper clad ground rod is computed as follows:

I = total current required for test sample
i = current density in ma/sq. ft.
A = total area of test sample
P = plate
r = rod
R_p* = total resistance of plate[2] =

$$90\%^{**}\left(\frac{\rho}{4\pi \cdot \frac{1.4}{\pi} \cdot s \cdot 2.54}\right)$$

s = 12 inches

R_r* = total resistance of 6 foot rod

$$= \frac{0.012\,\rho \log_{10} \frac{D}{a}}{L}$$

a = 5/16 inches
D = 3 feet
L = 6 feet

$I_p = i_pA_p$
$I_r = i_rA_r$

and for equal potential change to half-cell:

$$I_rR_r = I_pR_p$$

then:

$$(i_rA_r)R_r = (i_pA_p)R_p$$

or:

$$\frac{i_r}{i_p} = \frac{A_pR_p}{A_rR_r}$$

$$\frac{i_r}{i_p} = \frac{\frac{(2)\quad(.9)\rho}{4\pi \cdot 1.4 \cdot 12 \cdot 2.54}}{\left(\frac{.98}{6}\right)\left(.012\rho \log_{10} \frac{3 \times 12}{5/16}\right)}$$

$\frac{i_r}{i_p} = 2.61$ Ratio of current required by one inch rod and 12 inch square plate of the same material, and must be altered for use of different materials.

Table 2 presents the data obtained during the field test indicating the current required to protect:

a. Steel plate alone
b. Copper rod alone
c. Copper and steel couple

The potentials recorded are negative with respect to $CuCuSO_4$ half-cell, and were obtained using a potentiometer type voltmeter. Figure 2 is a plot of this information.

Measured steel potential = —.66 without current applied

Measured copper potential = —.23 without current applied

Potential change:

Change Steel	Change Copper
—.85	—.85
—.66	—.23
.19	.62

Ratio of change of potential $= \frac{.62}{.19}$

$= 3.26$

* Resistance determined to actual location of half-cell in field test for comparison purposes.
** Resistance at location of 5 times diagonal of plate equals 90 percent of resistance to remote location.

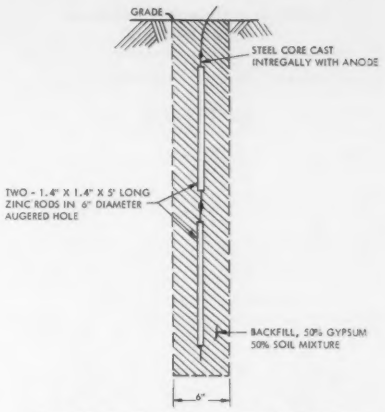
GRADE
STEEL CORE CAST INTREGALLY WITH ANODE
TWO - 1.4" X 1.4" X 5' LONG ZINC RODS IN 6" DIAMETER AUGERED HOLE
BACKFILL, 50% GYPSUM 50% SOIL MIXTURE
6"

Figure 3—Detail of zinc ground rod installation.

TABLE 1—Numerical Values of Current-Potential

Current, ma	Potential, volts
STEEL PLATE	
0	0.66
2.0	0.71
2.5	0.77
3.0	0.80
4.0	0.84
5.0	0.89
6.0	0.92
COPPER PLATE	
0	0.12
2.5	0.22
3.0	0.25
4.0	0.31
5.0	0.36
6.0	0.42
7.0	0.47
8.0	0.53
9.0	0.59
10	0.65
15	0.82
18	1.00
20	1.06
COPPER-STEEL COUPLE	
0	0.44
2.5	0.48
3.0	0.49
4.0	0.50
5.0	0.54
6.0	0.55
7.0	0.58
8.0	0.61
9.0	0.63
10	0.66
13	0.69
15	0.74
20	0.82
21.5	0.85
23	0.90
25	0.92

$$\frac{i_r}{i_p} = \frac{\frac{I_r}{A_r}}{\frac{I_p}{A_p}} = \frac{\frac{18}{.98}}{\frac{4}{2}} = 9.2.$$ Ratio of current required to overcome difference in potential and resistance

Ratio of current required due to the difference in resistance alone

$$= \frac{9.2}{3.26} = 2.82.$$ Determined from test measurement

TABLE 2—Numerical Values of Current-Potential

Current, ma	Potential, volts
COPPER ROD	
0	0.23
4.0	0.36
7.0	0.50
10	0.60
15	0.76
18	0.85
20	0.90
25	1.00
COPPER-STEEL COUPLE	
0	0.48
2.5	0.52
3.0	0.53
4.0	0.54
5.0	0.56
6.0	0.57
7.0	0.59
8.0	0.60
9.0	0.64
10	0.65
15	0.74
20	0.81
22	0.85
25	0.91
30	0.97

Ratio of current required due to difference in resistance alone

$$= 2.61$$

Determined by calculations

Results of Tests

From the analysis and field tests, it can be seen that for equal area and resistance under the same test conditions, it required as much as 3.75 times the current to raise the copper as steel to protective potentials, and is proportional to voltage change required for protection.

Further, the relative current density for different size pipes has a definite effect on the current requirements for a given potential change. This relative density is dependent upon the relative resistance of the structures.

It was realized that the exact current densities obtained in these tests would not hold true for the same metals buried in soil. However, it is reasonable to assume the relative ratio of currents required will be sufficiently accurate for estimating purposes.

For estimating purposes, it was assumed the average relative size of the underground pipe is 12 inches diameter and the copper ground is 1 inch diameter. Based upon the above computations, the ratio of current densities determined on relative resistance alone would be 8.59.

An "off" potential of —.65 was assumed for the steel and —.23 for the copper ground rod. The ratio of difference in the potential is then 2.8.

Then the ratio of current densities for 1 inch copper rod to 12 inch diameter steel pipe per square foot of area is 8.59 times 2.8 which equals 24.1.

It was assumed that it would require approximately 2 ma to raise the potential of 12 inch diameter steel in soil from —.65 to 0.85 volts. Utilizing the above factor of 24.1 and 2 ma current density to protect bare steel, the current required for the copper alone is estimated to be 2 ma $\times$ 24.1 $\times$ 5240 square of copper equals 253 amperes. It should be noted this figure is an estimate to approximate the magnitude of current required. The magnitude of the estimate becomes very significant when compared to the current estimated required to protect the underground metal in need of protection, which was estimated at 200 amperes. Should the copper system be installed in this particular case, over 50 percent of the current would flow to the copper which does not require protection.

It was obvious the cost of initial installation, maintenance and power due to the copper greatly increased the cost of cathodic protection at this location.

Elimination Of Copper

Various considerations were made to overcome the adverse effect of the copper, which included:

1. Elimination of the grounding system.

2. Isolation of the copper grounding system, and the metals to be protected.

3. Substitution of a less noble metal for the copper.

A brief review of each of the above means is in order at this point before consideration of the solution selected for this design.

1. Elimination of the grounding system. This is not possible since the electrical grounding is required for personnel safety, and to protect equipment from hazards of higher voltages.[3]

2. Isolation of copper grounding system. Copper grounding systems have been successfully isolated from structures to be protected. This has been accomplished on individual pipe lines, pipe type cables and isolated runs of lead covered cables, guy lines for overhead lines, etc. [4, 5] The isolation of the grounding system requires the use of certain low resistance insulating devices to provide paths for AC electrical fault currents. This method is limited to underground facilities which are not complex and interconnected at hundreds of locations. It is not considered practical or possible to employ this technique with a complex grounding system such as required for an industrial plant.

3. Substitution of a less noble metal for copper. Steel plates, galvanized steel rods and zinc ground rods have been reported to be successfully employed in the place of copper for grounds.[4, 5, 6, 7, 8] The National Electric Code[3] permits the use of both ferrous and non-ferrous metals for grounding purposes. The important factor to keep in mind when selecting metals for grounding is that the life of these metals buried in the ground is very important to ensure the safety offered by the grounding system is maintained. Cathodic protection has been employed to extend the life of steel or iron when used for grounding.

Selection Of Substitute Metal

The selection of an alternate metal for use in the electrical grounding systems was made to eliminate the excessive cathodic protection currents required by the copper. The various materials considered will not be covered here; however, the following items were paramount in the selection of the materials:

1. Long life in underground application.

2. Minimum demand upon cathodic protection system.

3. Cost.

4. Ease of installation.

5. Means of providing electrical connection to metal and insuring permanent connections.

The zinc ground rod was selected to replace the copper in the grounding system. Figure 3 is a detail of the typical zinc ground rod installation. The anodes are tied into the ground grid by use of insulated cables to eliminate exposed copper on the cable. The size selected was sufficient to provide the same resistance to ground as a 1 inch $\times$ 10 foot copper ground and its associated bare copper conductor. The life of the zinc anode, based on the American Zinc Institute[9] information, is in excess of 40 years without cathodic protection. The life will be materially increased by the application of cathodic protection to underground structures, since cathodic protection will greatly reduce the difference of potential between the zinc and other underground metals.

It is felt the choice of this material as a substitute for copper offers the following advantages and disadvantages:

Advantages:

a. Ease to design long life into the anode for soil application.

b. No demand on the cathodic protection system.

c. Anode will supply its own protection to cable connection to minimize connector problems.

Disadvantages:

a. Zinc anodes could not be driven into ground, and required separate augered holes for installation.

b. Zinc anodes were not available in 10 foot lengths, and required splicing two 5 foot anodes together.

c. In order to obtain most beneficial results, a special backfill was required around the anode.

The cathodic protection system was subsequently designed and installed with a total design current of 200 amperes. The cathodic protection system consists of three rectifiers and ground beds located at three spots selected around the plant. This provides cathodic protection to:

1. Bottom of the on-ground tanks, etc.

2. Underground tanks and associated piping.

3. Oxygen lines.

4. Acetylene lines.

5. Gas main.

6. Water main.

7. Underground cast iron fire and sprinkler main (joints of main were bonded during installation).

8. The building "H" piles were not provided cathodic protection. However, some small degree of protection is realized by bonds into the cathodic protection system and zinc ground electrodes.

The average "on" potential obtained at locations remote to the cathodic protection ground bed was — 0.93 volt with a total of 184 amperes flowing from the three rectifiers.

Conclusions

1. The copper grounding system effect must be considered in the design of cathodic protection.

2. Current requirements to raise the potential of the copper must be considered for the difference in potential it exhibits, and the resistance of the copper electrode compared to the structures to be protected.

3. Due to the possible serious corrosion problems caused by the copper grounding systems, consideration should be given to its effects in the design of any new facility.

4. The corrosion engineer can play an important role in co-ordination of electrical and mechanical designs. He can minimize corrosion by elimination of "built-in" corrosion problems, and reduce the cost of corrosion control measures.

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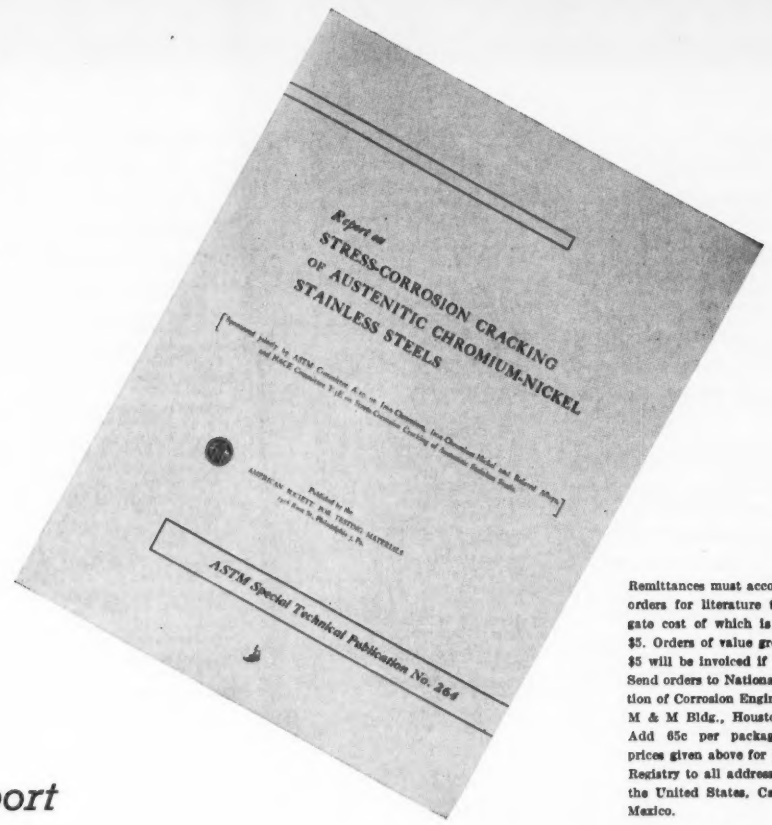

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